

bp 157° (740 mm), n_D^{25} 1.4309–1.4312 (lit.¹⁶ bp 153.5–154.5°, n_D^{20} 1.4341).

1-Ethyltetramethyldisiloxan-3-ol and Heptamethyltrisiloxan-3-ol.—Solvents and water were removed from the filtrates from reactions 16 and 17 on a rotary-film evaporator. Fractional distillation yielded the disiloxanol, 14.0 g, a 79% yield, bp 41–42° at approximately 1 mm, and the trisiloxanol, 20.8 g, an 85% yield, bp 50.5–57.5° at approximately 1 mm. Other properties and analyses were reported previously.¹⁷

Procedure for Reactions 1–3 in Table II.—See Table II for additional data on reagents, conditions, and yields.

Reactions 1 and 2.—In each reaction an *in situ* catalyst was prepared by heating 0.02 g (8.4×10^{-6} mole) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

(16) M. F. Shostakovskii, *et al.*, *J. Gen. Chem. USSR*, **24**, 2202 (1954); *Chem. Abstr.*, **50**, 3270 (1956).

(17) G. H. Barnes and N. E. Daughenbaugh, *Anal. Chem.*, **35**, 1308 (1963).

with 19.8 g (0.10 mole) of diphenylmethylsilane at 130–180° until the original green color passed through yellow and became black. After cooling to room temperature, the toluene was added, followed by either water in reaction 1 or buffered solution in reaction 2. The mixtures were heated under a reflux condenser for the time indicated in Table II. Tests for remaining Si–H by the mercuric chloride method were negative. The toluene layers were separated and dried, and the products were isolated by fractional distillation under vacuum.

Reaction 3.—The catalyst was prepared by adding dropwise a solution of 1.0 g (2.6×10^{-2} mole) of sodium borohydride in 20 ml of water to 4.0 g (1.68×10^{-2} mole) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 ml of water. The resulting black precipitate was washed once with water and once with dioxane and stored under dioxane until used.

Approximately 0.039 g of this catalyst was added to the flask containing the three other reagents and the remainder of the procedure closely followed the procedure for reactions 1 and 2.

On the Mechanism of Metal Chelate Catalysis in the Reaction between Alcohols and Isocyanates

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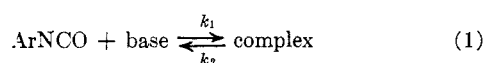
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Catalysis of the urethan reaction by ferric acetylacetonate [$\text{Fe}(\text{AA})_3$] can be described or predicted quantitatively if it is assumed that alcoholysis of the chelate is the first step in the reaction sequence. The validity of this assumption is demonstrated for the following systems: (1) undiluted hexanediiisocyanate and neododecanol, (2) *n*-butyl isocyanate and 1-butanol in benzene, (3) *n*-butyl isocyanate in excess 1-butanol, and (4) phenyl isocyanate in excess 1-butanol. The dependence of the rate constant on $\text{Fe}(\text{AA})_3$ concentration is parabolic, while the addition of small amounts of acetylacetone (HAA) to the metal-catalyzed reaction causes a hyperbolic response. Both phenomena are described quantitatively by a single equation.

Metal chelate catalysis of alcohol–isocyanate reactions, although widely used in industry, has found little attention in the literature. Very little is known about the mechanism of this catalysis. The few published mechanisms are adaptations of Baker's mechanism for base catalysis^{1–4}—the metal chelate essentially substituting the base.⁵

The mechanism proposed by Baker and co-workers is as shown in eq 1 plus 2 and, independent of this,



the uncatalyzed reaction shown in eq 3.



From the stationary state condition, the concentration of the complex is given by eq 4, and the rate of

$$\text{complex} = \frac{k_1[\text{ArNCO}][\text{base}]}{k_2 + k_3[\text{ROH}]} \quad (4)$$

formation of the product is obtained by eq 5.

$$\frac{d[\text{ArNHCOOR}]}{dt} = k_0(\text{ArNCO})(\text{ROH}) + \frac{k_1k_3[\text{ArNCO}][\text{ROH}][\text{base}]}{k_2 + k_3[\text{ROH}]} \quad (5)$$

The second-order rate constant is defined as follows.

$$\frac{d[\text{ArNHCOOR}]/dt}{[\text{ArNCO}][\text{ROH}]}$$

With this eq 5 reduces to

$$k_{bi} = k_0 + \frac{k_1k_3[\text{base}]}{k_2 + k_3[\text{ROH}]} \quad (6)$$

where k_{bi} = pseudo-second-order rate constant.⁶

If $k_2 \gg k_3[\text{ROH}]$, k_{bi} reduces to eq 7 in which $k_c =$

$$k_{bi} = k_0 + \frac{k_1k_3}{k_2} [\text{base}] = k_0 + k_c[\text{base}] \quad (7)$$

rate constant of the catalyzed reaction.

Later, other investigators adopted this mechanism by substituting the metal chelate for the base, thus deriving an analogous expression to eq 7, *i.e.*, eq 8,

$$k_{bi} = k_0 + k_c[\text{Fe}(\text{AA})_3] \quad (8)$$

where $\text{Fe}(\text{AA})_3$ = ferric acetylacetonate, a widely used metal chelate catalyst.

Results

Several observations cannot be explained by eq 8. The three more important ones are (1) a marked deviation from linearity of the rate constant with $\text{Fe}(\text{AA})_3$ concentration; (2) drastic reduction of catalytic activity by the addition of minute quantities of acetylacetone (HAA); and (3) addition of acids decreases while addition of bases increases the rate of the metal-catalyzed reaction.

(6) The prefix "pseudo" denotes that k_{bi} is not a true constant but rather a complex function of the concentration of the reactants and environment.

(1) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947).

(2) J. W. Baker and J. Gaunt, *ibid.*, 9 (1949).

(3) J. W. Baker and J. Gaunt, *ibid.*, 19 (1949).

(4) J. W. Baker, M. M. Davies, and J. Gaunt, *ibid.*, 24 (1949).

(5) L. Schieler, Technical Report No. 32-129, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., July 1, 1961.

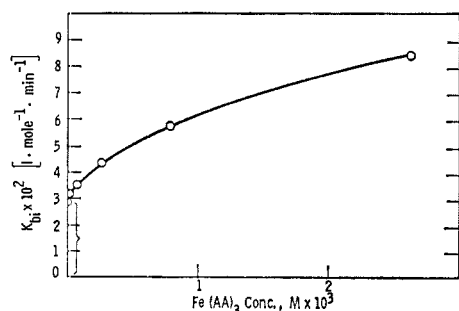


Figure 1.—Dependence of rate constant on catalyst concentration of PhNCO in excess BuOH.

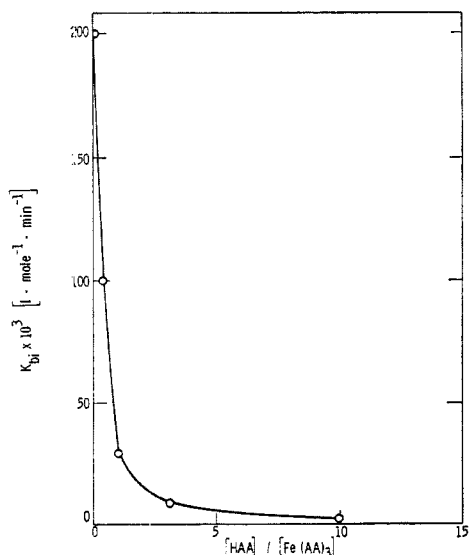


Figure 2.—Dependence of rate constant on the ratio of [HAA]/[Fe(AA)₃] in the reaction between BuOH and BuNCO in benzene.

Some representative data for these general observations are listed in Table I.

TABLE I
PSEUDO-SECOND-ORDER RATE CONSTANTS, k_{bi} , FOR THE REACTION BETWEEN BuNCO AND BuOH (0.7 M EACH) IN BENZENE, AND BETWEEN PhNCO AND BuOH (0.683 M EACH) IN BENZENE AT 25.5°

Additives	$M \times 10^3$	$10^4 k_{bi}$, l. mole ⁻¹ min ⁻¹ ^a
BuNCO-BuOH Reaction		
None	...	2.3
Fe(AA) ₃	2.62	4200
Fe(AA) ₃ , HAA	2.62, 2.62	100
HAA	2.62	3
Fe(AA) ₃ , CF ₃ COOH	2.62, 2.62	740
CF ₃ COOH	2.62	3.8
Dimethylpiperazine, Fe(AA) ₃	50, 2.62	5600
Dimethylpiperazine	50	7.0
PhNCO-BuOH Reaction		
None	...	180
Fe(AA) ₃	2.62	1700
Fe(AA) ₃ , HAA	2.62, 2.62	400
Dimethylpiperazine	2.62	340

^a In some reactions, particularly the uncatalyzed ones, the k_{bi} values were not constant but followed a trend. Therefore, the k_{bi} values at 50% reaction are listed.

The effect of HAA can only be explained by specific action on the catalyst, since its quantity is too small to block either of the reactants. It also exhibits a slight

catalytic activity when used alone. While acids have a mild catalytic effect on the urethan formation, their presence in Fe(AA)₃-catalyzed reactions results in a strong reduction of the rate.

Aliphatic isocyanates are particularly suitable for the investigation of metal catalysis owing to the large difference between the catalyzed and uncatalyzed reaction rate.

Figure 1 shows the parabolic dependence of k_{bi} on Fe(AA)₃ concentration. The parabolic dependence was obtained in all of the systems investigated. These follow: *n*-butyl isocyanate (BuNCO) and *n*-butyl alcohol (BuOH) in benzene, BuNCO in excess BuOH, phenyl isocyanate (PhNCO) in excess BuOH, and hexamethylene diisocyanate and 2,2-dimethyldecanol-1. The latter system was chosen because here the course of the reaction can be followed in a refractometer even in the undiluted mixture, since no crystallization of the diurethan takes place at room temperature. The same four systems were also used to determine the effect of HAA, which in all cases was hyperbolic. An example for the hyperbolic response is given in Figure 2.

Figure 3 shows the agreement between the experimentally determined rate constants and the k_{bi} values calculated from eq 15 (see Discussion). The constants "a" and "A" were obtained from eq 17. The rate constants are given in terms $\Delta n/\text{min}$, where Δn is the change of refractive index during reaction and is directly proportional to the decrease in concentration of the reactants. Table II lists the measured and cal-

TABLE II
CALCULATED AND MEASURED k_{bi} VALUES FOR THE Fe(AA)₃-CATALYZED REACTION BETWEEN PhNCO (0.677 M) IN EXCESS BuOH (10.06 M)^a

Fe(AA) ₃ , $M \times 10^3$	HAA, $M \times 10^3$	$10^4 k_{bi}$, l. mole ⁻¹ min ⁻¹	
		Obsd	Calcd
...	...	2.85	...
2.62	...	8.50	8.43
0.785	...	5.78	5.71
0.262	...	4.35	4.35
0.0785	...	3.50	3.53
0.0262	...	3.11	3.15
2.62	5.55	3.25	3.29
2.62	2.78	3.65	3.73
2.62	0.926	5.02	5.02
2.62	0.555	5.84	5.82
2.62	0.278	6.88	6.87

^a k_{bi} at 50% reaction; temperature, 25.5°; $A = 74$; $a = 6.35 \times 10^{-5}$.

culated values of k_{bi} for the reaction of phenyl isocyanate with *n*-butyl alcohol; Table III presents the same for butyl isocyanate and butyl alcohol in benzene. Good agreement between experimental and calculated values is obtained.

The two constants "A" and "a" of eq 15 should be valid for any concentration of Fe(AA)₃ or combination of Fe(AA)₃ with HAA as long as the system (concentration of alcohol, isocyanate, and the solvent) is not greatly changed. In Figure 4, curve 3 has been generated using the constants "A" and "a" calculated from the point of intersection of curve 1 with curve 2. Again, good agreement between theoretical and experimental values is demonstrated by data of Figure 4 and Table IV.

TABLE III

CALCULATED AND MEASURED k_{bi} VALUES FOR THE REACTION BETWEEN BuNCO AND BuOH, BOTH 0.7 M IN BENZENE^a

Fe(AA) ₃ , M × 10 ³	HAA, M × 10 ³	10 ³ k _{bi} , l. mole ⁻¹ min ⁻¹	
		Obsd	Calcd
...	...	0.02	...
7.86	...	60.5	62.5
2.62	...	32.0	35.0
0.786	...	16.5	18.6
0.262	...	10.2	10.25
0.0786	...	6.3	5.14
1.29	0.39	8.5	7.48
1.29	1.29	3.0	2.47
1.29	3.9	0.95	0.86
1.29	12.9	0.32	0.27

^a k_{bi} values at 30% reaction; temperature, 25.5°; $A = 982$; $a = 1.30 \times 10^{-5}$.

TABLE IV

MEASURED AND CALCULATED k_{bi} VALUES FOR THE REACTION BETWEEN BuNCO (0.645 M) IN EXCESS BuOH (10.06 M)^a

Fe(AA) ₃ , M × 10 ³	HAA, M × 10 ³	10 ³ k _{bi} , l. mole ⁻¹ min ⁻¹	
		Obsd	Calcd
...	...	0.02	...
2.62	...	8.25	8.91
1.57	...	6.50	6.83
0.786	...	4.63	4.76
0.262	...	2.72	2.64
0.157	...	2.15	1.99
0.0785	...	1.45	1.34
2.62	0.2	5.55	5.42
2.62	0.4	3.60	3.64
2.62	0.785	1.81	2.12
2.62	2.62	0.60	0.68
2.62	7.85	0.20	0.27
7.86	0.2	11.1	11.65
5.24	0.2	9.1	8.87
2.62	0.2	5.55	5.42
1.57	0.2	4.05	3.69
0.786	0.2	2.2	2.1
0.262	0.2	0.83	0.81

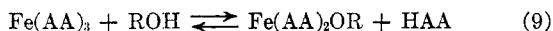
^a k_{bi} values at 50% reaction; temperature, 25.5°; $A = 241$; $a = 1.387 \times 10^{-5}$.

The parabolic dependence of k_{bi} on catalyst concentration and hyperbolic response of the metal-catalyzed reaction rate constant to HAA addition is not restricted to ferric acetylacetonate, but has been encountered by the authors with other metal acetylacetonates. Details of this work will be reported in the near future.

Discussion

It is desirable that any proposed mechanism of metal chelate catalysis should account for the observations listed at the beginning of the foregoing section.

The alcoholysis reaction of Fe(AA)₃, eq 9, accounts



quantitatively for the effect of varying Fe(AA)₃ and HAA concentration on the reaction rate, and at least qualitatively explains the effect of acids and bases on the rate of the metal-catalyzed urethan formation. For this it is necessary to assume that Fe(AA)₂OR is the activated species. From eq 9 it is readily seen that addition of HAA would suppress the formation of the complex, as well as that acids would cause a similar effect since they liberate HAA from Fe(AA)₃. Bases

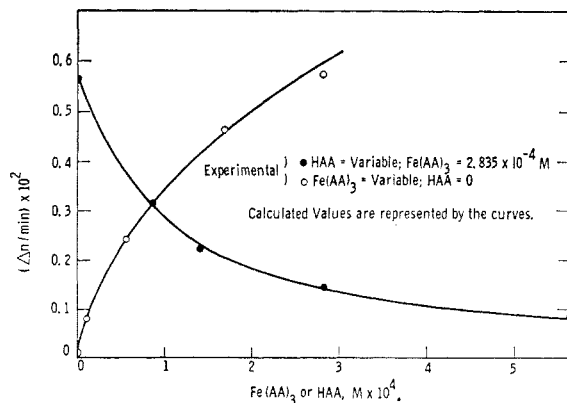


Figure 3.—Dependence of reaction rate of neododecyl alcohol with HDI on Fe(AA)₃ and HAA concentration (equivalent ratio of neododecanol to HDI = 1:1, no solvent; rates taken at 50% reaction). $dn/dt = B[\sqrt{(X+a)^2 + 4ac} - (X+a)] + D$. $X = \text{HAA concentration}$ and $c = \text{Fe(AA)}_3 \text{ concentration}$. $a = 1.04 \times 10^{-5}$; $B = 59.5$; $D = 0.01 \times 10^{-2}[\Delta n/\text{min}]$.

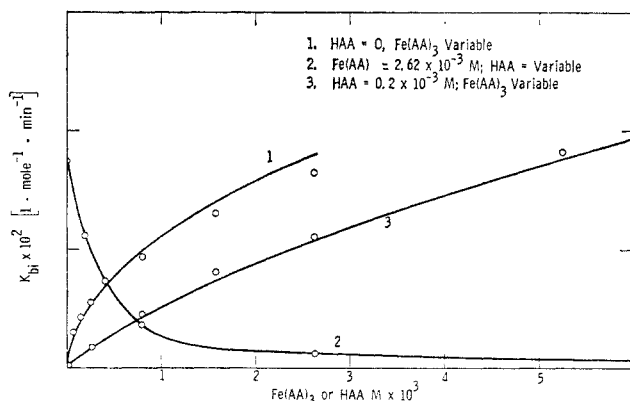
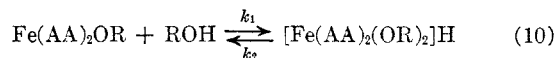


Figure 4.—Reaction rates of BuNCO (0.645 M) in excess BuOH (10.06 M) at 25.5° (K_{bi} values at 50% reaction).

favor the formation of the alkoxo complex through salt formation with the HAA, the latter being a weak acid.

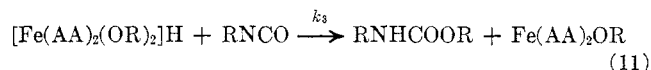
Reactions between metal halides and alcohols yielding so called alkoxo acids are known.⁷ Indeed, compounds of the type Fe(AA)₂OR have been prepared.⁸

The coordinatively unsaturated Fe(AA)₂OR probably adds another molecule of alcohol (eq 10). The



latter product has been formulated as complex acid in analogy to Meerwein's alkoxo acids.

Assume that reaction 9 is fast, that eq 10 represents the next step in the reaction sequence, and that the final step (11) regenerates the catalyst. Then ap-



plication of the steady-state condition to eq 10 and 11 yields a pseudo-second-order rate constant (eq 12).

$$k_{bi} = \frac{k_1 k_3}{k_2 + k_3[\text{RNCO}]} [\text{Fe(AA)}_2\text{OR}] + k_0 \quad (12)$$

(7) (a) H. Meerwein, *Ann. Chem.*, **455**, 227 (1927); **476**, 113 (1929); **484**, 113 (1930). (b) D. C. Bradley, *et al.*, *J. Chem. Soc.*, 3039 (1957); 3450 (1950); 2002 (1954).

(8) B. Emmert and E. Jacob, *Ber.*, **B67**, 286 (1934).

The concentration of $\text{Fe}(\text{AA})_2\text{OR}$, denoted as x , is calculated from eq 9 as in eq 13, where $\text{HAA} =$

$$\frac{(x)(\text{HAA} + x)}{(c - x)(\text{ROH} - x)} = K \quad (13)$$

acetylacetone added to reaction mixture in addition to the amount which is formed by the alcoholysis and $c = \text{Fe}(\text{AA})_3$ concentration prior to alcoholysis.

Since $\text{ROH} \gg x$, $(\text{ROH} - x)$ simplifies to ROH . Solving for x in eq 13 and substituting it in 12 yields

$$k_{bi} = k_0 + \frac{k_1 k_3 \{ \sqrt{([\text{HAA}] + K[\text{ROH}])^2 + 4K[\text{ROH}]c} - ([\text{HAA}] + K[\text{ROH}]) \}}{2(k_2 + k_3[\text{RNCO}])} \quad (14)$$

Equation 14 is of little practical value since none of the individual constants are known. However, if, *e.g.*, in a kinetic study of the effect of varying catalyst concentration on the reaction rate, the system (alcohol and isocyanate concentration and medium) remains unchanged, and if the rate data of the individual kinetic runs are compared at the same extent of the reaction, then $[\text{ROH}]$ and $[\text{RNCO}]$ can be treated as constants and eq 14 reduces to

$$k = k_0 + A \{ \sqrt{([\text{HAA}] + a)^2 + 4ac} - ([\text{HAA}] + a) \} \quad (15)$$

Equation 15 contains only two constants "A" and "a" (characteristic for the given system) and thus is more readily verified experimentally. It is easily seen that eq 15 represents a function which is hyperbolic for HAA [with $\text{Fe}(\text{AA})_3 = \text{constant}$] or parabolic for $\text{Fe}(\text{AA})_3$ (with $\text{HAA} = 0$ or constant).

In principle only two points on a curve showing the effect of varying $\text{Fe}(\text{AA})_3$ concentration [or HAA concentration at constant $\text{Fe}(\text{AA})_3$ concentration] on k_{bi} should suffice to allow the calculation of the constants A and a. In practice, however, it turns out that unless the k_{bi} values are of extreme accuracy the calculated constants will be in considerable error.

A practical route to obtain the two constants, A and a, is from the point of intersection of the curve representing the effect of varying $\text{Fe}(\text{AA})_3$ concentration, y (no added HAA), on k_{bi} (curve 1 of Figure 4) with the curve representing the effect of varying the HAA concentration, x (at a fixed catalyst concentration = c), on k_{bi} (curve 2 of Figure 4). Since at the point of intersection $(k_{bi})_1 = (k_{bi})_2$, it follows that

$$A[\sqrt{(x+a)^2 + 4ac} - (x+a)] + k_0 = A[\sqrt{a^2 + 4ay} - a] + k_0 \quad (16)$$

At the same time $x = y$ at this point. Substituting in eq 16 yields 16a and from this a simple algebraic

$$A[\sqrt{(x+a)^2 + 4ac} - (x+a)] + k_0 = A[\sqrt{a^2 + 4ax} - a] + k_0 \quad (16a)$$

relation for a is obtained

$$a = \frac{x^2}{c(c-x)} \quad (17)$$

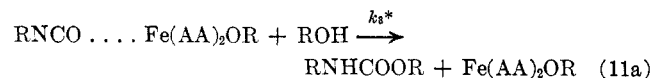
where x is the concentration of either $\text{Fe}(\text{AA})_3$ (for curve 1) or HAA (for curve 2) at the point of intersection.

Other Possible Variations.—In the systems studied, the alcoholysis (eq 9) is sufficient to explain the dependence of the reaction rate on $\text{Fe}(\text{AA})_3$ and HAA concentration. Whether the $\text{Fe}(\text{AA})_2\text{OR}$ adds an-

other molecule of alcohol, as shown before, or forms an activated complex with the isocyanate will be the subject of future work. Here we wish to show solely that such combinations lead to mathematically equivalent functions for the effect of catalyst and HAA concentration on the rate of the reaction. For example, $\text{Fe}(\text{AA})_2\text{OR}$ should possess a permanent dipole moment owing to its asymmetry, whereas $\text{Fe}(\text{AA})_3$ lacks a permanent dipole moment.^{9,10} Hence, an isocyanate is more likely to complex with $\text{Fe}(\text{AA})_2\text{OR}$ than with the nonpolar and coordinatively saturated $\text{Fe}(\text{AA})_3$. We may write



and



Applying steady-state condition we obtain eq 12a.

$$k_{bi}^* = \frac{k_1^* k_3^* [\text{Fe}(\text{AA})_2\text{OR}]}{k_2^* + k_3^* [\text{ROH}]} + k_0 \quad (12a)$$

Equation 12a differs from eq 12 merely by having $[\text{ROH}]$ in the denominator instead of $[\text{RNCO}]$ and thus can be reduced to eq 15. Other variations are possible by letting the individual reactions proceed at different rates, but a mathematical analysis shows that such assumptions lead to expressions which are equivalent to eq 15.

With the foregoing we hope to have shown that consideration of an alcohol-metal chelate complex as the active species in the catalyzed urethan reaction offers a better explanation of the observed kinetics than the assumption of an isocyanate-metal chelate complex. The first step in the reaction sequence, *i.e.*, alcoholysis of the metal chelate, is sufficient to describe quantitatively the effect of varying catalyst and HAA concentration on the rate of urethan formation. No firm conclusions on the further fate of the alkoxo compound can be drawn from the available data, but work on this subject is in progress.

Experimental Section

Materials.—*n*-Butyl alcohol and benzene were Bakers Analyzed Reagent grade chemicals. *n*-Butyl alcohol was further purified by refluxing over reagent grade CaO for 5 hr and distilling, bp 117.5–118°. Benzene was stored over Na wire and distilled before use, bp 80°. The phenyl isocyanate, Eastman, Cat. No. 553, was repeatedly fractionated over P_2O_5 , bp 56° (14 mm). Analysis showed 98.7% isocyanate. Butyl isocyanate, Eastman, Cat. No. P 7184, was found to contain small amounts of carbamyl chloride which tended to produce a mild catalysis. This impurity was not removed by the P_2O_5 treatment, as evidenced by a slight reduction of reaction rate when small amounts of a tertiary base were added. We then proceeded to reflux BuNCO with a long-chain tertiary amine (dimethyl-dodecylamine). Final fractionation over P_2O_5 yielded a product, bp 114°, which responded positively to base catalysis. Analysis indicated 99.3% isocyanate.

The ferric acetylacetonate from Mac Kenzie Chemical Works, Inc., was recrystallized twice by dissolving 5 g of $\text{Fe}(\text{AA})_3$ in 20 ml of warm benzene and adding 100 ml of hot heptane. On cooling, $\text{Fe}(\text{AA})_3$ crystallizes in dark red platelets, mp 184°. Hexamethylene diisocyanate, Mobay Chemical Co., was re-

(9) I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).

(10) J. Macqueen and J. W. Smith, *ibid.*, 1821 (1956).

distilled, bp 142° (21 mm), assay 98.7%. Neododecyl alcohol from Eastman was used as received.

Procedure.—The fast reactions (50% completion in less than 30 min) were run in 250-ml iodine flasks in 25-ml portions containing all ingredients except isocyanate. The reaction was begun by the addition with an automatic pipet of 2 ml of the isocyanate and stopped after a measured time by the addition of 5 ml of dibutylamine. Vigorous stirring kept the maximum temperature rise below 0.5°. Each flask yielded one point of the concentration–time curve. For these reactions, the error was generally less than $\pm 2\%$.

Slower reactions (50% reaction in more than 30 min) were run in a 1-l. flask with 275 ml of reaction mixture. After certain time intervals, 25-ml aliquots were transferred to erlenmeyer flasks containing a measured amount of dibutylamine in dioxane.

The unreacted isocyanate was determined by back titration of the excess dibutylamine¹¹ with 1 *N* HCl using a mixed indicator (0.075% bromocresol green and 0.025% methyl red in methanol) showing a sharp color change at pH 5.1. To maintain a homogeneous solution, 50 to 100 ml of methanol was added to the reactant mixture prior to titration. All reactions were run in a thermostat at 25.5° controlled by a TECAM TEMPUNIT (La Pine Scientific Co.) to $\pm 0.05^\circ\text{C}$.

The reaction of hexamethylene diisocyanate with neododecyl alcohol was followed in a water-cooled Abbe-3L refractometer (precision ± 0.0001) (Bausch and Lomb) at 25°. The linear dependence of refractive index on the concentration of reactants and formed urethan was experimentally established. The difference of the refractive index between the initial reaction mixture ($n_D^{25} 1.4445$) and the diurethan ($n_D^{25} 1.4613$) allowed an exact determination of the course of the reaction. The use of neododecyl alcohol permitted following the reaction to completion, since the diurethan did not crystallize at room temperature. The use of the refractometer had the advantage of positive temperature control which prevented exotherm of the urethan reaction.

The conversion of the experimental points to pseudo-second-order rate constants was achieved by drawing concentration *vs.* time curves. The tangents to the curves at these points were established with a mirror device. The rate constant for any point on the curve is then given by

(11) H. E. Stagg, *Analyst*, **71**, 557 (1946).

$$k_{bi} = \frac{\tan \alpha}{[\text{RNCO}][\text{ROH}]}$$

where $\tan \alpha = d[\text{RNCO}]/dt$. This procedure was adopted to obtain a more accurate "rate constant" than is possible by a $1/C$ *vs.* time plot or, in the case of unequal concentration of the two reactants, a plot of $1/(b-a) \ln [(a-x)/(b-x)]$ *vs.* time. The reason for this is that the rate constant of the urethan reaction is not a constant and varies with the extent of reaction and initial concentration of reactants and solvent. For example, Ephraim and co-workers¹² point out that, besides strongly affecting the absolute value of the "rate constant," both positive and negative deviations from the second-order plot occur if the solvent is changed; *i.e.*, the "rate constant" changes during the course of the reaction.

Similar observations are made on $\text{Fe}(\text{AA})_3$ -catalyzed reactions provided they are run in dilute solution in a solvent. When the solvent was excess BuOH, the k_{bi} value remained practically constant throughout the reaction (pseudo first order). In all solvents tested (benzene, toluene, heptane, dioxane, diethylene glycol dimethyl ether, methyl ethyl ketone, and acetonitrile), the rate constant increased with the extent of reaction. An example of this is given in Table V for reaction between BuOH (0.6 *M*) and BuNCO (0.6 *M*) catalyzed by $\text{Fe}(\text{AA})_3$ (2.62×10^{-3} *M*) in benzene at 25.5°.

TABLE V

Extent of reaction, %	k_{bi} , l. mole ⁻¹ min ⁻¹
10	0.368
20	0.391
30	0.386
40	0.412
50	0.453
60	0.497
70	0.528
80	0.522

For these reasons, the "rate constants" of the individual kinetic runs are compared at the same extent of reaction.

The over-all accuracy of the rate constants, as judged from repeat experiments, should be at least $\pm 10\%$.

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Thermal Decomposition of Copper and Silver Aryls in Aprotic Media¹

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The thermal decomposition of phenyl- and *p*-tolylcopper in ether suspension and of phenyl- and *p*-tolylsilver in ether suspension and in pyridine solution has been studied. Addition of *p*-benzoquinone suppressed the yield of hydrocarbons remarkably. A cross product was formed in a statistical ratio on the competitive decompositions in homogeneous media. Probable mechanisms are discussed.

The preparations and some reactions of copper aryls and silver aryls have been reported, for instance, by Gilman and Straley² and Starkey, *et al.*,³ but the thermal decomposition mechanism of these compounds does not seem to have been well characterized. Gardner and co-workers⁴ studied the action of silver bromide on a mixture of phenylmagnesium bromide and *p*-anisylmagnesium bromide and on mixtures of phenylmagnesium bromide and various alkylmagnesium bromides. They also studied the thermal decomposition of a mixture of *p*-tolylsilver and *p*-anisylsilver.

In all cases, all possible coupling products were formed and no evidence of reaction with solvent was found. They proposed that the decomposition of organosilver compounds is a bimolecular reaction of them rather than an interaction of free radicals formed initially.

As for alkylcopper and alkylsilver series, considerable work on their decomposition reactions has been performed by Semerano,⁵ Gilman,⁶ Bawn,⁷ and Costa,⁸

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