A Kinetic Study of the Dimerization of Phenyl Isocyanate

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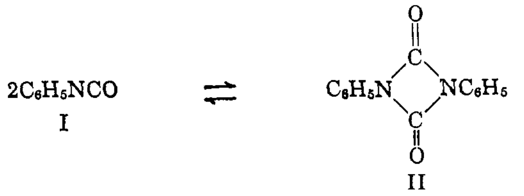
Abstract: The kinetics of the dimerization equilibrium of phenyl isocyanate (I) catalyzed by tributylphosphine have been studied in toluene as a solvent. The rate law observed was $d[\text{dimer}]/dt = (k_f[\text{isocyanate}]^2 - k_r[\text{dimer}])\cdot[\text{phosphine}]$. The rate constant for the forward reaction (k_f) was $(1.08 \pm 0.22) \times 10^{-3}$ l.^{2} mole^{-2} sec^{-2} at 35.0°, and that for the reverse reaction (k_r) was $(10.9 \pm 0.12) \times 10^{-3}$ l. mole^{-1} sec^{-1}. The equilibrium constant found at 35°, $K = 0.092$ l. mole^{-1}, was consistent with these rate constants. Equilibrium constants were measured at 5.0, 15.0, 25.1, 35.0, and 45.0°; rate constants were measured at all but 45°. The following thermodynamic functions were estimated for the dimerization (based on 1 mole of dimer formed in 1 l. at 25°): $\Delta H^* = 0.52 \pm 0.71$ kcal; $\Delta S^* = -70.3 \pm 2.7$ cal deg^{-1}; $\Delta H = -10.2 \pm 0.9$ kcal; $\Delta S° = -37.6 \pm 3.4$ cal deg^{-1}. No trimer (triphenyl isocyanurate or triphenyl-*s*-triazine-2,4,6(1H,3H,5H)-trione) could be detected by product isolation and infrared spectroscopy during the initial dimerization, but on long standing of the reaction mixture this product was formed. The results were consistent with a kinetically controlled, reversible formation of the dimer (1,3-diphenyl-2,4-uretidinedione, II) by way of a highly ordered transition state involving two molecules of phenyl isocyanate and one molecule of tributylphosphine.

The base-catalyzed conversion of phenyl isocyanate (I) to its dimer, 1,3-diphenyl-2,4-uretidinedione (II, eq 1), has been known since 1858.[2] The symmetrical uretidinedione structure for the dimer is considered to be the best representation on the basis of the crystal structure established[3] by three-dimensional X-ray analysis. Triethylphosphine was the first dimerization catalyst used,[2] and it is the one most often used with bulk isocyanate for the synthesis of II and the dimers of other aryl isocyanates.[4-8] Other trialkylphosphines have also been successful as catalysts.[9] Aryldialkylphosphines were found to be active catalysts, but the substitution of two aryl groups on the phosphorus atom greatly lowered catalytic activity.[10] Pyridine was much less active than tertiary phosphines, but it would cause dimerization when it was used as a solvent for aryl isocyanates.[11,12] No uncatalyzed dimerization of I or of other aryl monoisocyanates has been reported. On the other hand, 2,4-tolylene diisocyanate (4-methyl-*m*-phenylene diisocyanate) in the absence of added catalyst has been reported to dimerize slowly on standing[13] and to set up the unfavorable dimerization equilibrium at higher temperatures.[8] Dimerization of alkyl isocyanates has not been observed.[9] Attempts to catalyze such dimerizations with trialkylphosphines have led only to trimerization.[13]



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The only studies[8,14] on the kinetics of dimerization of isocyanates have involved initial rates of dimerization of bulk 2,4-tolylene diisocyanate. This dimerization either uncatalyzed[8] or catalyzed for ferric acetonylacetonate[14] was accompanied by trimerization. These oligomerizations were studied as relatively slow, undesirable side reactions which accompany the formation of polyurethans. The reverse of dimerization (dedimerization) of 2,4-tolylene diisocyanate has been reported in a review article[9] to be a first-order reaction, but no details were given.

In view of the limited availability of information which could be applied to a formulation of the dimerization mechanism, the present kinetic investigation on the dimerization of phenyl isocyanate (I) was undertaken.

Tributylphosphine was chosen as the catalyst for the kinetic studies. It was expected to be nearly as active in producing dimerization as triethylphosphine, and it had the advantages of lower volatility and lower cost. With I in toluene solution at 25.1° at constant catalyst concentration the reaction showed pseudo-second-order kinetics. This was determined by plotting log [initial rate] *vs.* log [I] where [I] is the concentration of isocyanate. A good, straight-line plot was obtained with a slope of 1.93 ± 0.10.

Examination of the later stages of these kinetic runs showed that the reaction rate decreased much too rapidly for the reaction to be described as simple second order. Indeed, the conversion to II stopped long before completion, indicating a reversible reaction in which equilibrium had been attained. The rate law (eq 2) was set up on the assumptions that the dimerization was a second-order reaction opposed by a first-order dedimerization, and that both steps were catalyzed by the phosphine. The integrated eq 3 was derived from this rate law and from the expression for the equilibrium constant.

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[1] Ethyl Corp. Predoctoral Fellow, 1963–1964.

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[13] J. H. Saunders and R. J. Slocombe, *Chem. Rev.*, **43**, 203 (1948).

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$$d[II]/dt = (k_f[I]^2 - k_r[II])[B] \qquad (2)$$

$$k_f[B]t = \frac{[II]_{eq}}{[I]_0^2 - 4[II]_{eq}^2} \ln \frac{[II]_{eq}([I]_0^2 - 4[II][II]_{eq})}{[I]_0^2([II]_{eq} - [II])} \qquad (3)$$

In these equations k_f and k_r are the rate constants for forward and reverse reactions, respectively; [I], [II], and [B] are concentrations of I, II, and catalyst, respectively, with the subscript 0 referring to initial concentration and the subscript eq referring to equilibrium concentration.

Graphical applications of eq 3 to the dimerization reaction gave good, straight-line plots of $k_f[B]t$ *vs.* t in all cases. In some cases, the reaction was followed to over 90% attainment of equilibrium. For most of the runs an effort was made to follow the reaction to over 75% attainment of equilibrium. This was impossible for runs at higher initial isocyanate concentrations, however, because of crystallization of the dimer product before equilibrium was that closely approached.

In toluene solution at 25.1°, when the initial isocyanate concentration was constant, the reaction rate showed first-order dependence on the tributylphosphine concentration. A plot of log [initial rate] *vs.* log [B] gave a good straight line with a slope of 1.02 ± 0.13. Third-order rate constants for the dimerization reaction obtained by dividing the pseudo-second-order constants by the catalyst concentration are given in Table I. These values of dimerization constants are much higher than those which can be estimated from the data given[8,14] for bulk 2,4-tolylene diisocyanate. On the basis of compatible concentration units, the uncatalyzed[8] dimerization at 40° had a constant of 3.3×10^{-10} l. mole^{-1} sec^{-1}, while that catalyzed by ferric acetonylacetonate[14] at 40° had a constant of 2.1×10^{-7} l.^{2} mole^{-2} sec^{-1}. Admittedly, the trialkylphosphine is a far more effective catalyst.

Table I. Rate Constants for the Dimerization of Phenyl Isocyanate (I)

$[C_6H_5NCO]_0$, *M*	$[\text{Catalyst}]_0$, *M*	Temp, °C	$k_f \times 10^3$ l.^{2} mole^{-2} sec^{-1}
0.397	0.062	25.1	1.18
0.597	0.062	25.1	1.12
0.791	0.062	25.1	1.15
0.991	0.062	25.1	1.15
1.397	0.062	25.1	1.10
0.792	0.025	25.1	1.14
0.792	0.101	25.1	1.17
0.796	0.062	35.0	1.18
0.792	0.025	35.0	0.98
0.786	0.050	15.0	1.18
0.591	0.050	15.0	1.12
0.589	0.050	5.0	0.97
0.391	0.050	5.0	0.95

Equilibrium constants for the dimerization of I were determined. They are given in Table II. The approach to equilibrium was relatively rapid and free from side reactions when the tertiary phosphine catalyst was used. The monomeric isocyanate was greatly favored at room temperature and above. No evidence for trimerization[6,9,13] was observed when the dimerization equilibrium was followed by product isolation and infrared spectroscopy. On long standing, however, the reaction mixtures showed evidence of trimer formation. A plot of log *K vs.* 1/*T* gave a good straight line and allowed calculation of the following thermodynamic properties (based on 1 mole of dimer formed in 1 l. at 25°): $\Delta H = -10.2 \pm 0.9$ kcal, $\Delta S° = -37.6 \pm 3.4$ cal deg^{-1}, $\Delta F° = 1.02 \pm 0.05$ kcal, where the measure of the precision sets the 95% confidence limits. From the data reported[8] for the extent of dimerization of 2,4-tolylene diisocyanate in bulk, it is possible to estimate the equilibrium constants in terms of the same units used for the data of Table II (l. mole^{-1}). The values obtained, 1.53×10^{-2} at 78° and 1.24×10^{-2} at 100°, are roughly comparable to those which would be predicted for the dimerization of I in toluene at these temperatures (0.013 and 0.005, respectively). For 2,4-tolylene diisocyanate the estimated values for ΔH (−2.3 kcal per mole of dimer formed) and $\Delta S°$ (−15 cal deg^{-1} per mole of dimer formed in 1 l.) over the temperature range 78–100° are of substantially lower magnitude than those given above for I over a somewhat lower temperature range. None of these data seem consistent with the equilibrium conversions (72% at 25° and 90% at 10°) of 2,4-tolylene diisocyanate to dimer in benzene solutions which were reported in a review article[9] with no details whatsoever about concentrations or the method of determination. Such equilibrium conversions would require impossibly high concentrations to be reasonably consistent. Besides, ΔH would have to be approximately −25 kcal per mole of dimer formed which is ten times the value reported[8] for bulk samples.

Table II. Equilibrium Constants for the Dimerization of Phenyl Isocyanate (I) in Toluene

Temp, °C	*K*, l. mole^{-1}
5.0	0.603
15.0	0.304
25.1	0.178
35.0	0.092
45.0	0.05

Several kinetic runs were made starting with pure II and tributylphosphine in toluene at 35.0°. At this temperature, initial concentrations of II on the order of 0.07 *M* could be attained, and the reaction could be expected to go nearly to completion. Treatment of this reaction as first order in dimer and approximately irreversible gave good agreement to about 75% completion. Plots of log [II] *vs.* *t* gave good straight lines. A value of $10^{-3}(10.9 \pm 0.12)$ l. mole^{-1} sec^{-1} was obtained for the second-order rate constant (k_r) for this reverse reaction. This with the value of $k_f = 10^{-3} \cdot (1.08 \pm 0.22)$ leads to the prediction of an equilibrium constant of 0.100 ± 0.015 at 35° which checks well with the value (0.092) given in Table II and which fits as well as that value on the linear plot of log *K vs.* 1/*T*.

Dedimerization reactions were also attempted using pyridine, tributyl phosphite, triphenylphosphine, N-methylmorpholine, and triethylamine. Although solvent and temperature conditions were the same as for the runs using tributylphosphine, none of these catalysts produced any measurable amount of dedimerization reaction. On the other hand, in N-methylmorpholine as a solvent a 62% yield of trimer was obtained from II in 15 min at 115°. In view of the fact that pyridine and tributyl phosphite will catalyze the forward reaction for I in bulk isocyanate, it must be concluded that they will also catalyze the reverse reaction if concentrations and temperatures are high enough. Triphenylphosphine was ineffective in catalyzing the dimerization of I in bulk, and triethylamine and N-methylmorpholine led to the formation of trimer.

Rate constants for the reverse reaction (k_r) were calculated from the values of k_f (Table I) and the equilibrium constant (Table II). Plots of log k *vs.* $1/T$ gave straight lines and allowed the determination of Arrhenius activation energies, E_a, for both forward and reverse reactions. Values for the enthalpy, entropy, and free energy of activation were calculated for both the forward and reverse reactions and are summarized in Table III.

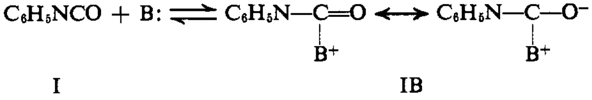
Table III. Activation Parameters for the Dimerization Based on 1 Mole of Dimer II Formed in 1 l. at 25°

	Dimerization[a]	Dedimerization[a,b]
E_a	1.12 ± 0.71 kcal	11.6 ± 0.9 kcal
ΔH^*	0.52 ± 0.71 kcal	11.0 ± 0.9 kcal
ΔS^*	−70.3 ± 2.7 cal deg^{-1}	−31.0 ± 3.0 cal deg^{-1}
ΔF^*	21.5 ± 1.5 kcal	20.4 ± 2.0 kcal

[a] The precision sets the 95% confidence limits of the averages. [b] The rate constants (k_r) used were calculated from the rate constant of the forward reaction (k_f) and the equilibrium constant (K).

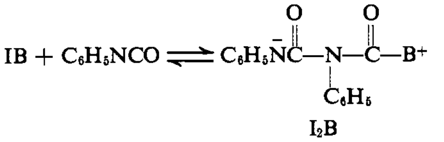
From the kinetic data reported for the uncatalyzed dimerization[8] and for the dimerization catalyzed by ferric acetylacetonate,[14] it is possible to estimate the activation parameters per mole of the dimer of 2,4-tolylene diisocyanate formed per liter at 40° for comparison with the results in Table III. For dimerization ΔH^* is 20 kcal uncatalyzed and 19 kcal catalyzed; ΔS^* is −37 cal deg^{-1} uncatalyzed and −29 cal deg^{-1} catalyzed. For dedimerization ΔH^* is 23 kcal uncatalyzed and 21 kcal catalyzed; ΔS^* is −22 cal deg^{-1} uncatalyzed and −14 cal deg^{-1} catalyzed. The higher enthalpies of activation (ΔH^*) compared with the results of Table III are not surprising since trialkylphosphines are considered to be the best catalysts for dimerization. The lower magnitude of the negative entropy of activation would be expected for the uncatalyzed reaction, but the still lower magnitude in the case of the dimerization catalyzed by ferric acetonylacetonate suggests a loss of order in going from the highly ordered chelate to the catalyst as it becomes associated in the transition state.

On the basis of kinetic data, the following mechanism is reasonable for dimerization catalyzed by tributylphosphine.



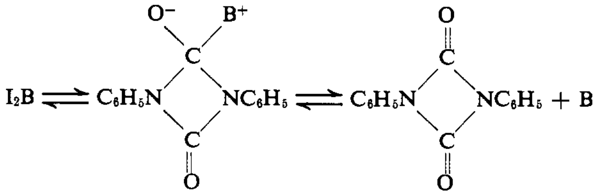
$$C_6H_5NCO + B: \rightleftharpoons C_6H_5\overset{-}{N}{-}\underset{B^+}{C}{=}O \longleftrightarrow C_6H_5N{-}\underset{B^+}{C}{-}O^- \qquad (4)$$

I IB



$$IB + C_6H_5NCO \rightleftharpoons C_6H_5\overset{-}{N}\overset{\overset{O}{\|}}{C}{-}\underset{C_6H_5}{N}{-}\overset{\overset{O}{\|}}{C}{-}B^+ \qquad (5)$$

I$_2$B



(6,7)

II

Step 4 involves the equilibrium formation of isocyanate–catalyst complex IB. The complex IB, now containing a nucleophilic nitrogen atom, then attacks a molecule of isocyanate to form intermediate complex I$_2$B. Cyclization and ejection of the base then results in dimer formation and regeneration of the catalyst, as in steps 6 and 7. The structure IB is the most likely one for the isocyanate–catalyst complex. The carbonyl carbon of the isocyanate is the site most susceptible to attack by nucleophilic or basic reagents, and the resulting complex would be stabilized by conjugation. In further support of this structure, the addition compounds of triethylphosphine with phenyl isothiocyanate and diphenyl ketene have been assigned[15] the inner salt structures analogous to IB. These compounds are crystalline substances, insoluble in water, but soluble in dilute acid. Similar adducts with I have not been isolated, but it is not unreasonable to assume that an equilibrium of the type in step 4 is set up in solution. Such intermediates have been suggested for base-catalyzed reactions of isocyanates such as urethan formation,[16] polymerization,[17] and even dimerization,[9] except that in the last-named case the steps which followed the formation of IB were different from those outlined above.

The kinetics indicate that step 4 is a rapid unfavorable equilibrium and that one of the following steps is relatively slow. Step 6 might be assigned as the slow step on the basis of the high negative entropy of activation, which indicates a marked ordering in the transition state. However, if step 6 is slower than step 5, then higher polymeric products might be expected since all propagation steps involving attack of a complex such as IB or I$_2$B on an isocyanate molecule might be expected to take place at roughly the same rate. Actually, a concerted dimerization involving some combination of steps 4, 5, and 6 might best explain the kinetically preferred formation of the dimer when tributylphosphine is the catalyst. Further studies of dimerization and trimerization will be necessary to clarify this point.

Experimental Section

Materials. The phenyl isocyanate (I) used in the kinetic runs was Eastman reagent grade and was purified for use by three fractional distillations at reduced pressure. A small quantity of phosphorus pentoxide was added before the last fractional distillation, and the fraction boiling at 62.0–62.5° (20 mm) was collected. Pure I was stored under nitrogen in a tightly stoppered flask in a desiccator.

The tributylphosphine catalyst was obtained from K & K Laboratories. Three fractional distillations, the last from barium oxide, were necessary for purification and drying. The fraction boiling at 127–128° (21 mm) was collected and stored under nitrogen in a desiccator.

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(15) W. C. Davies and W. P. Walters, *J. Chem. Soc.*, 1786 (1935); L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).

(16) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, **9**, 31 (1949).

(17) V. E. Shashua, W. Sweeny, and R. F. Tietz, *J. Am. Chem. Soc.*, **82**, 866 (1960).

A 1500-ml sample of commercial toluene was shaken for a 5-min period in a 2000-ml separatory funnel with each of two 100-ml portions of concentrated sulfuric acid. The sample was then washed with 200-ml portions of water followed by three of dilute sodium hydroxide and three 200-ml portions of distilled water. The toluene which had been dried over anhydrous calcium chloride was finally distilled from sodium and kept in a bottle over sodium wire. For cases in which the toluene was used as a solvent for reactions involving tertiary phosphines, nitrogen was bubbled through the sample to remove oxygen.

Piperidine, bp 105–106° (745 mm), pyridine, bp 114–115° (745 mm), and tributyl phosphite, bp 135–136° (20 mm), were distilled from barium oxide before use.

The nitrogen used in the purification of toluene, for the storage of reagents, and for maintaining oxygen-free conditions during kinetic runs was Linde high-purity dry nitrogen. It was passed through aqueous basic pyrogallol, concentrated sulfuric acid, and a mixture of calcium sulfate and potassium hydroxide pellets in that order at the time it was used.

Phenyl isocyanate trimer prepared from I in triethylamine solvent was crystallized from toluene to give a product, mp 285–287°.

Preparation of 1,3-Diphenyl-2,4-uretidinedione (II). A solution of 45 ml (49.1 g, 0.41 mole) of I in 50 ml of dry toluene was placed in a small, round-bottomed flask. After addition of 4.0 ml (3.26 g, 0.016 mole) of tributylphosphine, the flask was stoppered tightly. White crystals started to form in the flask almost immediately after the addition of catalyst and a considerable amount of heat was evolved. The mixture was allowed to stand for 2 days. The product was then filtered, washed with cold ethanol, and dried in the atmosphere. A yield of 35.7 g (73%) of II was thus obtained. Two recrystallizations from toluene gave large white plates, mp 176–177°. The melting point and infrared spectrum agreed with the literature data[9] for II.

In the absence of solvent, phenyl isocyanate (30.0 ml, 32.4 g, 0.272 mole) was treated with five drops of tributylphosphine. Heat was evolved and the reaction mixture solidified within 30 min. A 30.5-g (94%) product was isolated as described above after the reaction had continued overnight.

In another experiment, a mixture of 21.6 ml (23.8 g, 0.20 mole) of I and 30.0 ml of anhydrous pyridine was allowed to stand at room temperature. At the end of 48 hr, the white, crystalline material present was separated from the light yellow solution by filtration and washed with dry toluene. Recrystallization from toluene gave 3.91 g (16.5%) of dimer, mp 176–177°.

In a similar experiment 10 ml (10.8 g, 0.091 mole) of I was mixed with 5 ml (4.84 g, 0.029 mole) of triethyl phosphite. No immediate change was noted. After 3 days, the white solid material in the solution was removed by filtration, washed with cold, dry toluene, and dried in the atmosphere. A 2.23 g (21%) yield of II (mp 176–177°) was obtained.

Similar experiments with triphenylphosphine, phosphorus trichloride, or tetrabutylammonium iodide gave no isolable amounts of II.

Conversion of Dimer to Trimer. A mixture of 4.49 g (0.0189 mole) of II and 10.0 ml of dry N-methylmorpholine was heated gently at 115° for 15 min. The mixture was cooled in an ice bath and filtered. The solid product was washed with cold 95% ethanol. The yield was 2.76 g (62%) of the trimer, mp 283–285°. Infrared spectra and the melting point of a mixture with an authentic sample confirmed its identity.

Analytical Procedure. A modification of the method of Baker and Holdsworth[18] was used for the determination of I in toluene solution. Piperidine (1 *M* in acetone) was prepared from 10 ml of dry piperidine in pure, dry acetone diluted to 100 ml total volume. The procedure for analyzing an unknown solution for I was as follows: dry toluene (10 ml) was pipetted into a 125-ml erlenmeyer flask fitted with a ground-glass stopper. The solvent was cooled in an ice bath and exactly 5 ml of the 1 *M* piperidine in acetone was added to the flask by pipet. A carefully measured 5- or 10-ml sample of the isocyanate solution to be analyzed was then added to the solution by pipet, and the mixture was allowed to stand for 20 min in the ice bath to allow complete formation of the urea. Then 25–50 ml of 95% ethanol was added from a buret, and the solution was swirled to bring the urea into solution. When all the urea had dissolved exactly 10 ml of the 0.5 *M* hydrochloric acid–ethanol solution was added from a buret. After the addition of 3 drops of the 0.1% bromocresol green and 1 drop of the 0.2% methyl red, the excess hydrochloric acid in the mixture was back titrated with 0.5 *M* sodium hydroxide solution; the first light blue-green coloration was taken as the end point.

Blank determinations were run in exactly the same manner except that isocyanate solutions were excluded from the procedure. Comparison of the amount of sodium hydroxide solution required by the blank with that amount required by the isocyanate solution enabled the calculation of the unknown isocyanate concentration by eq 8, where v is the volume of sodium hydroxide required by the sample, v_b is the volume of sodium hydroxide required by the blank, V is the volume of the sample in ml, and M is the molarity of the sodium hydroxide solution. Solutions of I, made up by weight, analyzed for at least 99.4% of their theoretical concentration by this method.

$$[\mathrm{I}] = M(v - v_b)/V \tag{8}$$

The piperidine–acetone and hydrochloric acid–ethanol solutions of the concentrations described were adequate for use in the analysis when the concentration of I in the unknown solutions did not exceed 1.0 *M*. For the analysis of solutions in which the concentration of I exceeded 1.0 *M*, the concentrations of the piperidine and hydrochloric acid solutions were raised to 1.5 and 0.75 *M*, respectively.

The presence of tertiary phosphines in the unknown solution obscured the otherwise sharp bromocresol green–methyl red end point. This was alleviated during the analysis of dimerization mixtures by adding 1 ml of 30% hydrogen peroxide after the addition of the standard hydrochloric acid solution and before the final titration with sodium hydroxide. The tertiary phosphine present was thus converted to a phosphine oxide which did not affect the end point.

Since II also reacted with piperidine to form a substituted biuret,[9] the analysis of dimerization mixtures gave the total concentration of I plus II. Solutions containing only II could be accurately analyzed by exactly the same procedure as that used for I and by use of an equation analogous to eq 8. When both I and II were present eq 9 was used if the initial solution contained only I, while eq 10 was used if the initial solution contained only II.

$$[\mathrm{I}] = 2M(v - v_b)/V - [\mathrm{I}]_0 \tag{9}$$

$$[\mathrm{II}] = 2[\mathrm{II}]_0 - M(v - v_b)/V \tag{10}$$

Kinetic Runs. All reaction vessels and apparatus used for the transfer of I were dried prior to use by storage overnight in an oven at 120°. Pipets used in making up reaction mixtures and in withdrawing samples were calibrated by weight with the solvent toluene.

In most cases, 200-ml volumetric flasks were used as reaction vessels. For kinetic runs in which the reaction was followed for more than several hours, the reaction vessel was protected from moisture by means of a glass tube 1.25 in. in diameter. This tube was tapered at one end so that it just fit over the mouth of the flask. It was held in a position concentric with the neck of the flask and attached to it by means of a short length of large-diameter rubber tubing. Anhydrous calcium sulfate was placed in the base of the tube around the neck of the flask. A piece of glass rod fused to the stopper of the flask served as an extension handle and allowed removal of the stopper for sampling purposes when the protecting tube was in place. The tube extended about 2 in. above the mouth of the flask and was kept stoppered with a large cork or rubber stopper.

A measured amount of I was placed in the reaction vessel and diluted with pure, dry toluene. The reaction vessel was then placed in a water bath maintained at 25.10 ± 0.02, 35.00 ± 0.02, or 45.00 ± 0.02° by means of a Sargent Thermo-Controller. A Wilkens-Anderson Lo-Temp refrigeration unit was used to control the bath at 5.0 ± 0.1 and at 15.0 ± 0.1°. After reaching temperature equilibrium, the solution was diluted to volume with pure solvent. In order to determine the original isocyanate concentration, 25 ml of solution was withdrawn from the reaction vessel. This amount provided two samples which were analyzed for I. The values obtained were used to calculate the initial concentration of I in the reaction mixture.

A second, dry, 200-ml volumetric flask, previously swept out with dry nitrogen, was weighed, and the desired amount of tributylphosphine was added by pipet. After the flask was weighed again, the phosphine was diluted with dry, oxygen-free toluene. When temperature equilibrium was reached in the water bath, the solution was diluted to volume.

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[18] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947).

The dimerization reaction was initiated by the addition of 25 ml of the tributylphosphine solution to the reaction vessel. The time at which half the amount of catalyst solution had been delivered from the pipet was noted and recorded as t_0. The flask was removed from the water bath and agitated vigorously for 20 sec to ensure thorough mixing of the reactants. To follow the disappearance of reactant with time, samples were removed from the reaction vessel by pipet and analyzed for I and II.

In kinetic runs in which the initial concentration of I was large, crystallization of II occurred before the equilibrium concentration of I could be reached. In such cases, the reaction was allowed to proceed until equilibrium of I with the saturated solution of II was attained, but no quantitative data were considered after the precipitation had started. The solid was identified as II in several such experiments. In one such case, the equilibrium mixture was allowed to stand for 48 hr. A 6.5% yield of the trimer (mp 281–283°) was isolated when the solid was removed by filtration at 45°.

Dimerization rate constants were measured at 5.0, 15.0, 25.1, and 35.0°. They are summarized in Table I. No meaningful results were possible at 45.0° because of the unfavorable equilibrium at that temperature.

Studies of the dedimerization reaction were made at 35.0°. At this temperature the reverse of dimerization is more rapid than at 25°, and the solubility of II in toluene allowed concentrations around 0.07 *M*. A weighed amount of pure, dry II was placed in a 200-ml volumetric flask and 150 ml of dry toluene was added. The mixture was warmed on a hot plate. After all of dimer II had dissolved, more toluene was added, and the solution was placed in the constant temperature bath at 35.0°. After the solution was diluted to 200 ml, 25 ml of the solution was removed and analyzed for II. To initiate the dedimerization reaction, 25 ml of tributylphosphine solution, prepared as described for the dimerization reaction, was added to the reaction vessel. The appearance of I was followed by removing samples from the reaction vessel and analyzing them as described above. Pyridine, N-methylmorpholine, tributyl phosphite, and triphenylphosphine were used as catalysts in other dedimerization runs. The procedure was the same as that described for tributylphosphine.

Determination of Equilibrium Constants. In an experiment similar to a kinetic run, a solution approximately 1 *M* in I and 0.06 *M* in tributylphosphine was made up in a 200-ml volumetric flask and placed in the water bath at the desired temperature. Dimerization proceeded until considerable crystalline product had appeared in the flask. Samples from the mixture were analyzed until they showed no further decrease in concentration of I. In this way, the concentration of I in equilibrium with a saturated solution of II was measured. Equation 11 was used to calculate this concentration of I.

$$[\mathrm{I}] = M(v - v_\mathrm{b})/V - [\mathrm{II}]_\mathrm{sat} \qquad (11)$$

In a separate experiment, a saturated solution of II was prepared from excess II in 100 ml of boiling toluene. It was allowed to crystallize while in the water bath at the desired temperature. The solution was then analyzed for the concentration of II in the saturated solution. These solubilities at various temperatures are summarized in Table IV.

Table IV. Concentrations of Dimer II in a Saturated Toluene Solution

Temp, °C	g/100 ml	$M \times 10^2$
5.0	0.64	2.69
15.0	0.828	3.48
25.1	1.29	5.42
35.0	1.81	7.62
45	...	9.8[a]

[a] Value estimated by extrapolation.

The combination of experiments allowed the determination of the concentration of II present in a saturated solution and the concentration of I in equilibrium with that solution of II at the same temperature. From these data the dimerization equilibrium constant could be calculated. This technique had the advantage of allowing a direct measurement of the concentration of II at equilibrium and made an accurate determination of the initial concentration of I unnecessary. Dimerization equilibrium constants were measured at 5, 15, 25, 35, and 45°. They are summarized in Table II.

In a separate series of experiments, initial concentrations of I were controlled such that equilibrium was reached before crystallization of II occurred. The analyses of I and II were carried out as before. Equilibrium constants calculated from these data agreed well with those determined by the method above.

Spectrophotometric Measurements. Preliminary experiments were carried out on the dimerization reaction of I in which the concentrations were followed by means of infrared absorption spectra. The measurements were carried out in 0.1-mm cells on a Perkin-Elmer Model 21 spectrometer. The characteristic bands used were the most intense in the spectra; the antisymmetric stretching band of the isocyanate group at 2280 cm^{-1} for I, the carbonyl stretching band at 1790 cm^{-1} for II, and the carbonyl stretching band at 1710 cm^{-1} for the trimer.

No reliable reaction rates nor equilibrium constants could be measured by spectrophotometric means. Various product mixtures could be identified and analyzed semiquantitatively by this method, however. At concentrations suitable for measuring spectra (*ca.* 10^{-2} *M*) no appreciable reaction was observed with either pyridine or triethylamine as a catalyst. At higher concentrations small amounts of trimer could be detected in diluted samples. Tributylphosphine reacted with carbon tetrachloride to give a dark red product of unknown constitution. In methylene chloride no such reaction was observed. Solutions containing 0.7 *M* I and various concentrations of tributylphosphine in methylene chloride slowly lost isocyanate as small concentrations of II first developed and then later increasing concentrations of the trimer developed. At 25° a dimerization equilibrium constant of 0.1 could be estimated from these data.

A solution of 1.15 g (4.8×10^{-3} mole) of II in 20 ml of pyridine was allowed to stand. Samples (2 ml) of this solution diluted with 30 ml of carbon tetrachloride showed disappearance of II and appearance of I to the extent of about 20% in 30 hr. No such reversal could be detected with the trimer.