The Conversion of Isocyanates into Carbodiimides with Isopropyl Methylphosphonofluoridate as Catalyst. Kinetic Studies[1a]

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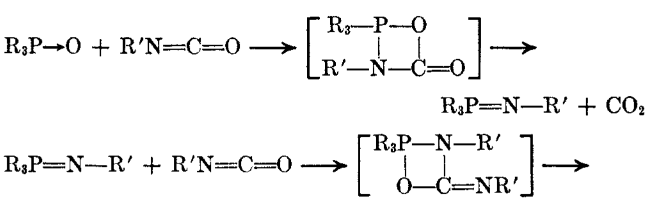
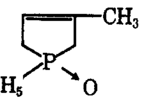
The catalysis of aryl isocyanates to carbodiimides by isopropyl methylphosphonofluoridate is shown to exhibit pseudo-zero-order kinetics in the absence of solvent at 135°. Second-order rate constants for the evolution of carbon dioxide are correlated by a Hammett plot and the first-order dependency on catalyst is demonstrated. The rates of carbon dioxide evolution and diphenylcarbodiimide formation from phenyl isocyanate and catalyst are found to be essentially equal, providing information on the rate-determining step.

The kinetics of carbon dioxide evolution from the conversion of isocyanates to carbodiimides catalyzed by 1-ethyl-3-methyl-3-phospholene 1-oxide (I) have been reported[2] in detail with the proposed reaction mechanism shown in Scheme I. This mechanism indicates that any pentavalent phosphorus compound which has a coordinate covalent bond between phosphorus and oxygen will catalyze the conversion reaction, and that the degree of catalytic activity will be dependent on the polarity of the phosphoryl bond and the steric hindrance around the phosphorus atom. In previously reported studies on the reaction of phenyl isocyanate with phosphate, phosphonate, phosphoramidate, and phosphine oxide catalysts, the diphenylcarbodiimide product was isolated, but the yield or rate of reaction was not correlated with the structure of the catalyst.[3]

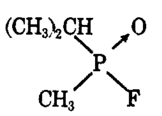
SCHEME I



In the present work, isopropyl methylphosphonofluoridate (II) was used as a catalyst. In light of the above mechanism, this compound should act as a catalyst, although a poor one, owing to the low polarity of the phosphoryl bond and the steric effect of the isopropyl group.



I



II

The rate constants for the conversion of phenyl isocyanate to the carbodiimide have been determined by following the diphenylcarbodiimide formation as well as the carbon dioxide evolution. The kinetic dependency of this reaction on catalyst concentration was established by a comparison of the rate constants at three concentrations. The rates of carbon dioxide evolution from a series of substituted aryl isocyanates were determined using the same fluorophosphonate (II) catalyst. Second-order rate constants for *meta* and *para* isomers were correlated using a Hammett plot, while the effect of steric hindrance in the isocyanate was investigated by a comparison of the rates obtained in experiments using the *ortho* and *para* isomers.

Results and Discussion

The isopropyl methylphosphonofluoridate catalyst used in the present study differs electronically and sterically from the cyclic phosphine oxide. The cyclic phosphine oxide would seem to have less steric hindrance for approach to the phosphorus–oxygen coordinate bond, and the alkyl substituents have a minimum electronic effect on this highly polarized linkage. In contrast, the bulky isopropoxy group on the fluorophosphonate makes approach of the isocyanate difficult, and the fluorine substituent as well as the oxygen of the isopropoxy group depolarize the coordinate bond to a great extent.[4] However, if the proposed mechanism is generally applicable and operative in this case, the slow catalytic reaction should exhibit pseudo-zero-order kinetics when the isocyanate is used as a solvent for the reaction.

The evolution of carbon dioxide from phenyl isocyanate catalyzed by II does exhibit pseudo-zero-order kinetics in the absence of solvent at 135°, as evidenced in Figure 1 by the straight-line plot of carbon dioxide concentration *vs.* time. In this figure, a plot of diphenylcarbodiimide concentration *vs.* time is also shown to be a straight line for a second catalyst concentration. In Figure 2, the reaction of phenyl isocyanate with catalyst II is shown to be first order in catalyst for both products by a plot of zero-order rate constants *vs.* catalyst concentration. An activation energy of 12.6 kcal/mole was calculated from the slope of the Arrhenius plot shown in Figure 3 which agrees with catalyst I data.[2]

From both the proposed mechanism and from experimentally observed pseudo-zero-order kinetics, it would be predicted that the first step of the reaction is rate determining, and, thus, the rate of carbodiimide formation should be equal to the rate of carbon dioxide evolution. The rate constants obtained for the evolution of carbon dioxide and the formation of diphenylcarbodiimide using three different catalyst concentrations are given in Table I. From this, the second-order

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[1] (a) This investigation was supported by the U. S. Army Edgewood Arsenal, Edgewood Arsenal, Md., under Contracts DA 18-108-405-CML-828 and DA 18-035-AMC-104(A). (b) To whom requests for reprints should be sent.

[2] J. J. Monagle, T. W. Campbell, and H. F. McShane, Jr., *J. Am. Chem. Soc.*, **84**, 4288 (1962).

[3] J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).

[4] (a) J. V. Bell, *et al.*, *J. Am. Chem. Soc.*, **76**, 5185 (1954); (b) E. L. Wagner, *ibid.*, **85**, 161 (1963).

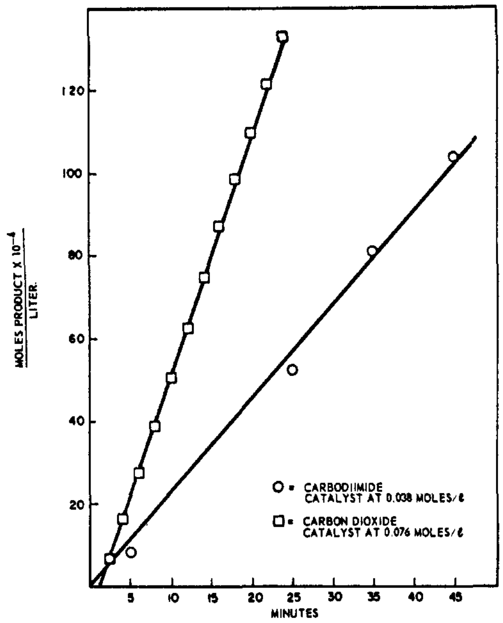

Figure 1.—Product concentration *vs.* time for phenyl isocyanate with catalyst II, 135°.

TABLE I

RATE CONSTANTS FOR CO_2 EVOLUTION AND $C_6H_5N{=}C{=}NC_6H_5$ FORMATION FROM PHENYL ISOCYANATE AT 135°

Catalyst, mole/l.	CO_2, $k_0 \times 10^5$ moles/l. sec	N=C=N, $k_0 \times 10^5$ moles/l. sec	CO_2, $k_2 \times 10^5$ l./mole sec	N=C=N, $k_2 \times 10^5$ l./mole sec
0.150	1.96	1.98	1.6	1.6
0.150	2.00		1.6	
0.076	0.98	0.93	1.6	1.5
0.076	0.90		1.4	
0.038	0.50	0.45	1.6	1.4
0.038	0.45	0.38	1.4	1.2
0.038	0.45		1.4	

constants for carbon dioxide evolution and diphenylcarbodiimide formation are shown to agree within the experimental error.

As with the cyclic phosphine oxide reaction, the fluorophosphonate-catalyzed conversion of isocyanates is enhanced by electron-withdrawing substituents on the benzene ring of the isocyanate. Second-order rate constants for a series of substituted phenyl isocyanates with catalyst II are given in Table II. These are correlated by a Hammett plot of σ substituent values[5] *vs.* log k, shown in Figure 4. A ρ value of +1.44 has been obtained at 135° in bulk isocyanates, compared with that of +1.25 at 110° in toluene[2] with catalyst I.

Steric hindrance in the isocyanate has a large effect on the reaction rate with catalyst II, as shown in Table III by comparison of the rate constants obtained for *ortho* and *para* isomers. Combined steric and inductive effects observed in the present study are similar to those previously found with catalyst I. For example, the ratio of the reaction rate of the *o*-chloro isomer to the *o*-methyl isomer is about 8 with catalyst II and 7 with I.

In summary, the generality of the proposed mechanism[2] for the formation of carbodiimides from the catalyzed conversion of isocyanates by a pentavalent organophosphorus compound is supported by the results reported above. Even though catalysts I and II have diverse activities toward isocyanates because of their widely different steric and electronic properties, the results of these and other[2] kinetic studies on both compounds are qualitatively very similar. The rate constants for I and II catalysis, found to differ by several orders of magnitude, are also consistent with the proposed mechanism.

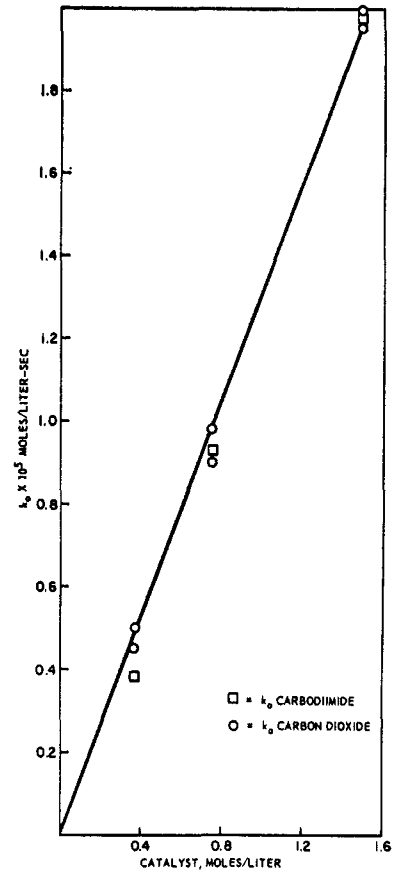

Figure 2.—Pseudo-zero-order rate constants *vs.* catalyst concentration.

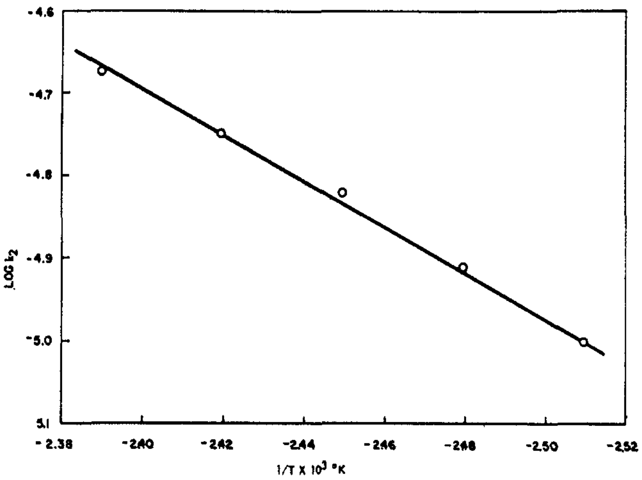

Figure 3.—Arrhenius plot for phenyl isocyanate with catalyst II.

Experimental Section

Materials.—The isocyanates were purified by distillation or sublimation before use. Isopropyl methylphosphonofluoridate[6]

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[5] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87.

[6] This compound was obtained from U. S. Army Edgewood Arsenal, Edgewood Arsenal, Md., and is extremely toxic and should be handled in a hood.

Table II

Rate Constants[a] for $2RC_6H_4NCO \rightarrow RC_6H_4N{=}C{=}NC_6H_4R + CO_2$ at 135°

R	σ	$k_2 \times 10^5$ l./mole sec	NCO, moles/l.	Catalyst, moles/l.	Registry No. Isocyanate	Registry No. Product
p-CH_3O	−0.268	1.20	6.92	0.069	5416-93-3	10076-13-8
p-CH_3	−0.170	0.92	7.04	0.071	622-58-2	726-42-1
m-CH_3	−0.069	0.90	7.28	0.073	621-29-4	726-28-3
H	0	1.54	8.25	0.076	103-71-9	622-16-2
p-Cl	0.227	2.61	7.30	0.074	104-12-1	838-98-2
p-Br	0.232	3.28	7.12	0.069	2493-02-9	726-41-0
m-Cl	0.373	3.53	7.43	0.076	2909-38-8	7778-12-3
m-NO_2	0.710	15.2	7.42	0.073	3320-87-4	10076-22-9
p-NO_2	0.778	17.3	6.83	0.068	100-28-7	738-66-9

[a] Average of at least two duplicate runs.

Table III

Rate Constants for CO_2 Evolution from *ortho*- and *para*-Substituted Isocyanates, RC_6H_4NCO

R	$k_2 \times 10^5$ l./mole sec	NCO, moles/l.	Catalyst, moles/l.	Registry No.
o-CH_3O	0.18	7.00	0.076	700-87-8
p-CH_3O	1.20	6.92	0.069	
o-CH_3	0.15	7.25	0.076	614-68-6
p-CH_3	0.92	7.04	0.071	
o-Cl	1.56	7.48	0.105	3320-83-0
p-Cl	2.61	7.30	0.074	

was distilled on a spinning-band column, with the fraction boiling at 45° (10 mm), dried, and stored over Drierite. The diphenylcarbodiimide used for chromatographic calibration was prepared by dehydrosulfurization of thiocarbanilide with mercuric oxide,[7] and purified distillation at 103–105° (0.1 mm).

Kinetic Procedure.—All reactions were carried out in a 100-ml flask equipped with a water condenser, thermometer or thermocouple, magnetic stirrer, and a small port fitted with a self-sealing rubber septum. Dry nitrogen was bubbled into the reaction mixture through a hypodermic needle in the septum, at a flow rate of 60 ml/min. A known volume or weight of isocyanate was introduced into the flask and brought to the desired reaction temperature, after which the catalyst was injected through the septum with a syringe. In all cases, a large excess of isocyanate was used as solvent, so that its concentration remained essentially constant throughout the sampling period. The densities of the isocyanates were measured to ±2% at 135° so that the reaction volumes and concentrations of reactants could be determined.

To analyze for carbon dioxide, the nitrogen stream from the reaction was passed through a 4.4-ml gas-sampling valve on a Perkin-Elmer Model 154-D gas chromatograph with a 2 m × 0.25 in. silica gel column at 126°. Samples were introduced into the chromatograph every 2 min, and the number of moles of carbon dioxide per sample was read directly from a linear calibration curve of moles carbon dioxide *vs.* peak height. The calibration was obtained by injecting known volumes of pure carbon dioxide into the chromatograph under the same conditions as those used in the analyses. Assuming that the rate of carbon dioxide evolution was constant in the 2-min interval between samples, the number of moles of carbon dioxide produced in any 2-min interval was calculated using the formula (moles of CO_2)/(4.4 ml of sample) × 60 ml./min × 2 min. The concentration of carbon dioxide at any time (t) was then determined by summing all the sample intervals up to time t, and dividing the total by the reaction volume.

To determine the amount of diphenylcarbodiimide formed from phenyl isocyanate in time t, liquid samples (2 μl) were withdrawn at 10-min intervals and analyzed on an F & M Model 720 programmed-temperature gas chromatograph, using a hydrogen flame detector. A 2 ft × 0.25 in. silicon gum rubber column (10% SE-30 on inert support) was used with the following chromatograph conditions. Flow rates were helium, 137 ml/min; hydrogen, 42 ml/min; oxygen, 280 ml/min. Temperatures were injection port, 230°; detector block, 240°. The column was programmed at 20°/min from 150 to 200°, with an initial isothermal period of 1 min. The chromatograph was calibrated using solutions of known molarity of diphenylcarbodiimide dissolved in phenyl isocyanate or benzene. The calibration plot of peak area *vs.* moles of carbodiimide was linear in the range 0 to 25 × 10^{-8} mole, which included all reaction samples.

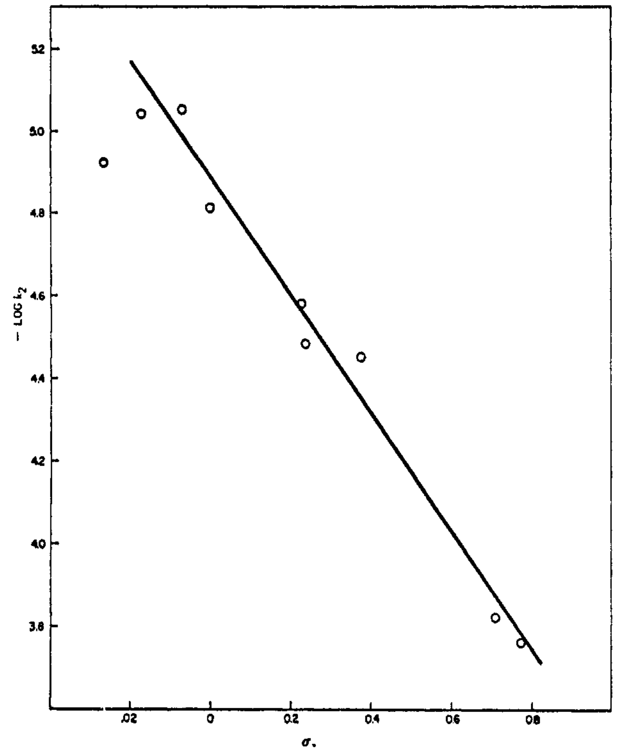

Figure 4.—Hammett plot (T = 135°, ρ = +1.44).

Plots of carbon dioxide or carbodiimide concentration *vs.* time were straight lines, the slope of which gave pseudo-zero-order rate constants. Second-order rate constants were calculated by dividing the slope by the concentrations of the reactants.

Registry No.—II, 107-44-8; carbon dioxide, 124-38-9.

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(7) L. J. Roll and R. Adams, *J. Am. Chem. Soc.*, **54**, 2494 (1932).