The Chemistry of Sulfonyl Isocyanates. VI. Pyridine Catalysis of the Reaction with Triphenylmethanol[1]

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p-Toluenesulfonyl isocyanate (I) reacted with triphenylmethanol (II) in toluene solution in the presence of pyridine to give N-(triphenylmethyl)-*p*-toluenesulfonamide (III) and carbon dioxide. The products were the same as in the uncatalyzed reaction. Pyridine caused a marked increase in the rate of CO_2 evolution. The catalyzed reaction was found to be first order in I and first order in II. The apparent second-order rate constant was dependent upon the concentration of pyridine up to at least 2 mol of pyridine/mol of I or II. A mechanism for the pyridine-catalyzed reaction is proposed.

It was shown in this laboratory that sulfonyl isocyanates, when allowed to react with triphenylmethanol and many other triarylcarbinols, gave the corresponding N-(triarylmethyl)sulfonamides and carbon dioxide.[2] The uncatalyzed reaction of benzenesulfonyl isocyanate with triphenylmethanol was extensively studied and was found to be first order in both isocyanate and carbinol.[3]

Graf reported the formation of tertiary amine complexes of sulfonyl isocyanates.[4] The complexes gave the same reactions as did the free isocyanates, although no rate studies were carried out. It was also reported that, upon addition of primary alkyl amines to tertiary amine complexes, a new set of complexes was formed which should give the corresponding sulfonylureas upon heating.[5,6] Tertiary amine complexes of sulfonyl isocyanates reacted with primary amine hydrochlorides to afford sulfonylureas and tertiary amine hydrochlorides.[7]

Burkus and Eckert found that triethylamine catalyzed the reactions of diisocyanates and 1-butanol in toluene solution.[8] Many solid complexes of tertiary amines and sulfonyl isocyanates, as well as tertiary amine–primary amine–sulfonyl isocyanate adducts, have been prepared and characterized.[6]

In this paper we show the results which we have obtained from the kinetic study of the reaction of *p*-toluenesulfonyl isocyanate (I) with triphenylmethanol (II) in the presence of pyridine. The rate of the reaction was followed by measuring the carbon dioxide evolved.[3] The effect of pyridine on the reaction between phenyl isocyanate and II is also shown.

We found earlier that the uncatalyzed reaction of phenyl isocyanate and II proceeded very slowly and gave N,N′-diphenyl-N-(triphenylmethyl)urea (IV).[2,9] We now report the effect of pyridine on this reaction at various reactant ratios and temperatures.

Experimental Section

Reagents.—*p*-Toluenesulfonyl isocyanate (I) was obtained from the Upjohn Co., Carwin Organic Chemicals, and was freshly distilled before use. Triphenylmethanol (II) and phenyl isocyanate were commercial products. Toluene was dried over sodium before use and pyridine was dried over solid potassium hydroxide.

Kinetics.—The method employed was similar to that reported earlier.[3] The separate solutions of I and II were prepared in 40 ml each of dry toluene in 50-ml volumetric flasks. To the solution of isocyanate was added the pyridine, whereupon a white solid precipitated. Pyridine, I, and II were all weighed to the nearest 1.0 mg. The flasks were immersed in an oil bath thermostated to ±0.1° and allowed to reach temperature equilibrium. The isocyanate–pyridine complex dissolved in hot toluene. More toluene was added to give a volume of 50 ml. The two solutions were saturated with dry CO_2 and rapidly mixed in a three-necked round-bottomed flask which was preheated in the constant-temperature bath and connected by a capillary to a gas buret. The volume of CO_2 was corrected for temperature and pressure (including the vapor pressure of toluene) and converted into moles. The latter was assumed to be the amount of isocyanate or carbinol consumed, and therefore calculated on the basis of moles/liter.

For the reactions using 1:1 ratio of isocyanate/carbinol, plots of $1/(c - c_\infty)$ (where c = calculated isocyanate or carbinol concentration at time t, and c_∞ = concentration at time infinity) *vs.* time were made. For other reactant ratios (4:1 to 1:4), linear plots were obtained from log $[b(a - x)]/[a(b - x)]$ *vs.* time.

Isolation of Product.—The isolation procedure for the product, N-(triphenylmethyl)-*p*-toluenesulfonamide (III), was identical with that described for N-(triphenylmethyl)benzenesulfonamide.[3]

Phenyl Isocyanate, II, and Pyridine.—Phenyl isocyanate (1.84 g, 0.015 mol), triphenylmethanol (II, 2.00 g, 0.0078 mol), and pyridine (5.92 g, 0.075 mol) were dissolved in dry toluene (5 ml) in a test tube. The test tube was stoppered with a cork and allowed to stand at room temperature for 24 hr. The resulting white precipitate was collected by suction filtration and washed with cold benzene, yield 1.27 g (80%), mp 232–233°, mmp 234–235° with N,N′-diphenylurea (V).

In another reaction an 8:1:8 ratio of isocyanate/II/pyridine heated for 3 hr at 100° gave the trimer (VI, 73%) of phenyl isocyanate, mp 277–280°.

Results

p-Toluenesulfonyl isocyanate (I) and triphenylmethanol (II) reacted at 100° in toluene to give the product N-(triphenylmethyl)-*p*-toluenesulfonamide (III). The product was the same whether pyridine was used or not.[2] The reaction of I and II was first order in isocyanate and first order in carbinol over at least two half-lives. Second-order plots gave straight lines in both the uncatalyzed and catalyzed reactions. The reaction was followed by measuring the evolved carbon dioxide.[3] The first 5–10% of reactions were

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(1) Taken in part from the Senior Theses of D. G. and W. H., DePauw University, 1967.

(2) J. W. McFarland, D. E. Lenz, and D. J. Grosse, *J. Org. Chem.*, **31**, 3798 (1966).

(3) J. W. McFarland, D. E. Lenz, and D. J. Grosse, *ibid.*, **33**, 3514 (1968).

(4) R. Graf, German Patent 1,000,807 (1957); *Chem. Abstr.*, **54**, 1555 (1957).

(5) Z. Brzozowski and W. Zacharewiz, *Rocz. Chem.*, **36**, 291 (1962); *Chem. Abstr.*, **57**, 16448 (1962).

(6) H. Ulrich, *Chem. Rev.*, **65**, 369 (1965).

(7) W. Anmuller and R. Weyer, German Patent 1,100,618 (1961); *Chem. Abstr.*, **55**, 24680 (1961).

(8) J. Burkus and C. F. Eckert, *J. Amer. Chem. Soc.*, **80**, 5948 (1958).

(9) Further and unpublished work in this laboratory showed that a better yield (67%) of IV may be obtained if C_6H_5NCO and II are heated at 100° for only 1 day and at a 2:1 reactant ratio, rather than 4 days as in ref 2.

followed using different reactant ratios, and eq 1 was employed for initial rates[10] (where n_A is the order of reagent A,

$$n_A = \frac{\log (dx/dt)_1 - \log (dx/d_2)_2}{\log [A]_1 - \log [A]_2} \qquad (1)$$

$(dx/dt)_1$ and $(dx/dt)_2$ are the rates for two different reactions, and $[A]_1$ and $[A]_2$ are the corresponding initial concentrations of reagent A). The order was found to be unity for both I and II in pyridine-catalyzed reactions.

As can be seen in Table I and in Figure 1, the presence of pyridine in the reaction solution caused a marked increase in reaction rate at 100°. The reaction was also studied at 85° and pyridine showed the same sort of rate enhancement as it did at 100°.

TABLE I

REACTION OF *p*-TOLUENESULFONYL ISOCYANATE (I) WITH TRIPHENYLMETHANOL (II) AT 100° (INITIAL CONCENTRATION OF I AND II = 4.358×10^{-2} *M*)

Initial pyridine concn, $M \times 10^2$	CO_2 evolved at 10.2 min, ml	CO_2 evolved at 15.1 min, ml
0	5.0	8.0
1.13	10.9	13.9
2.26	21.0	30.0
3.39	30.6	40.8
4.39	34.5	44.5
6.60	39.5	52.0
9.00	47.0	59.5

Although no rate studies were carried out at room temperature, pyridine caused the reaction of I and II to proceed smoothly at this temperature. This was in marked contrast to the uncatalyzed reaction, which required several days to give any substantial amount of product.

Unlike the sulfonyl isocyanate, phenyl isocyanate does not react with II in the presence of pyridine to give a product containing alcohol. Rather, pyridine catalyzes the competing reactions of phenyl isocyanate to give urea and the trimer. With a 2:1:10 ratio of isocyanate/II/pyridine at room temperature, the product was N,N′-diphenylurea (V) in 80% yield. With greater amounts of isocyanate (ratio 8:1:8), the trimer of phenyl isocyanate was obtained in good yield (73%). Inasmuch as tertiary amines are known to catalyze the conversion of isocyanates into trimers, the latter reaction is not surprising. The formation of urea, however, under anhydrous conditions probably involves participation of the carbinol in some fashion.

Discussion

In the uncatalyzed reaction between a sulfonyl isocyanate and a triarylcarbinol, it was proposed that the first step in the reaction was complex formation between the reactants.[3] The complex was then hypothesized to give an ion pair, one ion of which was the triarylcarbonium ion. Evidence for the existence of carbonium ions was that the reaction solutions absorbed at about 420 mμ. In the pyridine-catalyzed reactions there is also a buildup of a species which absorbs at 420–430 mμ.[11] Therefore, it might be concluded that a common intermediate is associated with catalyzed and uncatalyzed reactions.

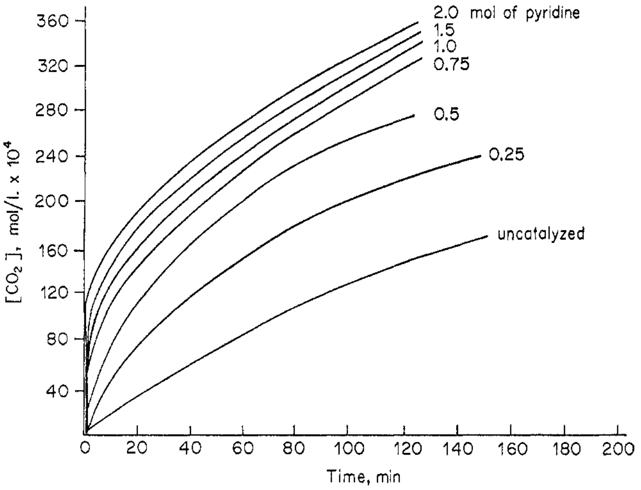
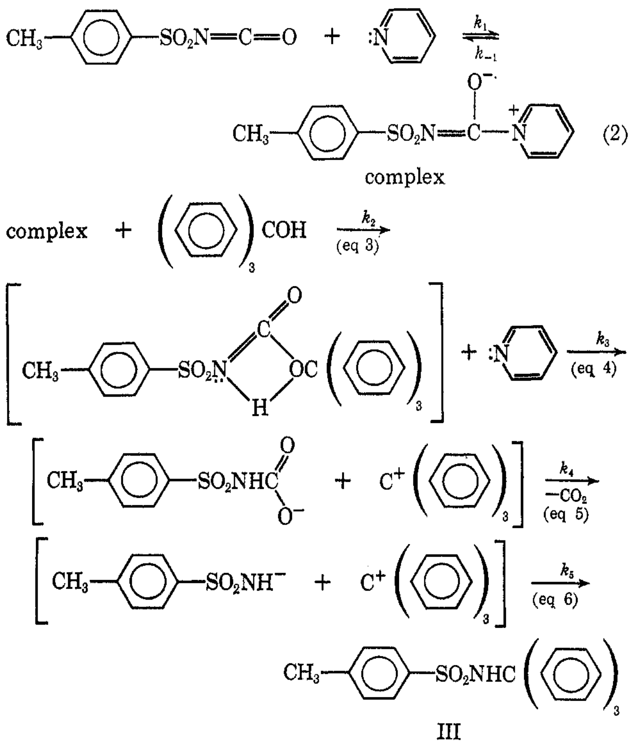


Figure 1.—Reaction of *p*-toluenesulfonyl isocyanate (I) with triphenylmethanol (II) at 100° in toluene with varying amounts of pyridine per mole of isocyanate or carbinol.

The facts that isocyanate–pyridine complexes have previously been found and that a precipitate is observed when isocyanate and pyridine are mixed indicate that a complex is formed and that it reacts with the carbinol. The question then arises as to why the reaction is faster with pyridine. A possible answer is that the pyridine forms a complex with isocyanate which is more easily attacked by carbinol. The following mechanism (2–6)



III

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[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, p 45.

[11] Attempts to follow the catalyzed reaction by the titration method[3] in order to determine the difference in isocyanate disappearance and the CO_2 evolution were not too successful. Pyridine appeared to interfere with the titration. Indications were that isocyanate disappeared slightly faster than CO_2 was evolved.

is, therefore, proposed for the catalyzed reaction. What we show as isocyanate–alcohol intermediate could, of course, be unstable urethan (see paper VII).[12]

The formation of a complex and subsequent attack by carbinol is somewhat analogous with a mechanism proposed by Baker and Gaunt for the reaction of phenyl isocyanate and alcohols.[13] Those workers proposed that isocyanate forms a complex with the first molecule of alcohol and the complex is then attacked by another molecule of alcohol. It was also found that the apparent second-order rate constant was dependent upon initial alcohol concentration.

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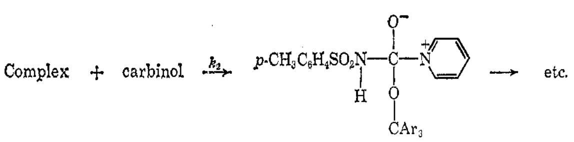
[12] A reviewer suggested that the isocyanate-pyridine complex reacts with carbinol to form an intermediate with a good leaving group. The intermediate loses pyridine to give urethan, which further decomposes.



[13] J. W. Baker and J. Gaunt, *J. Chem. Soc.*, **151**, 19 (1949).

The Chemistry of Sulfonyl Isocyanates. VII. Kinetics of the Reactions with Substituted Triphenylmethanols

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4-Toluenesulfonyl isocyanate (I) reacted with triphenylmethanol (II) and substituted triphenylmethanols at 100°. The products were N-(triarylmethyl)-4-toluenesulfonamides and CO_2, except that tris(4-nitrophenyl)-methanol gave the urethan. A kinetic study revealed that the reactions obeyed second-order kinetics, first order in isocyanate and first order in carbinol. The relative rates of reaction were $(4\text{-}CH_3OC_6H_4)_3COH$ > $(4\text{-}C_6H_5C_6H_4)_3COH$ > $(C_6H_5)_3COH$ > $(4\text{-}ClC_6H_4)(C_6H_5)_2COH$ > $(4\text{-}NO_2C_6H_4)(C_6H_5)_2COH$ > $(4\text{-}NO_2C_6H_4)_2(C_6H_5)COH$ > $(4\text{-}NO_2C_6H_4)_3COH$. The results were correlated according to a modified Hammett function.

It has been shown in this laboratory that sulfonyl isocyanates react with triarylmethanols to give in most cases the corresponding N-(triarylmethyl)sulfonamides.[2-4] The kinetics of the reaction between benzenesulfonyl isocyanate or 4-toluenesulfonyl isocyanate (I) and triphenylmethanol (II) were studied.[3,4] The reactions were first order in each of the reagents in cases of the uncatalyzed and pyridine-catalyzed reactions.

A mechanism was proposed for the above reaction which consisted of the intermediate formation of a complex between isocyanate and carbinol. The complex was then hypothesized to decompose to an ion pair, one of the ions being triphenylmethyl carbonium ion.

This paper records the results which were obtained by using substituted triphenylmethanols in their reactions with I. It was of interest to determine what effect substituents would have on the rates of reactions. The reaction rates were followed by measuring the disappearance of isocyanate.

Experimental Section

Reagents.—4-Toluenesulfonyl isocyanate (I) was obtained from the Upjohn Co., Carwin Organic Chemicals, and used without further purification. Triphenylmethanol (II) was a commercial product. Tris(4-methoxyphenyl)methanol (III), tris-(4-biphenylyl)methanol (IV), (4-chlorophenyl)diphenylmethanol (V), and tris(4-nitrophenyl)methanol (VI) were prepared as indicated before.[2] The other triarylmethanols were prepared as shown below. Toluene was reagent grade and dried over sodium before use. The di-*n*-butylamine was Eastman White Label grade reagent.

Kinetics.—The method used for measuring isocyanate concentration was similar to that already reported.[3] The only two modifications follow. Instead of removing 2-ml samples, *ca.* 2 ml of sample was removed and weighed. This was accomplished by weighing the 10 ml of di-*n*-butylamine solution to the nearest 0.5 mg before and after adding the aliquot. For the conversion of weight into volume, it was assumed that the density of solution was the same as the density of pure toluene solvent at 100°. *Ca.* 1.0 g of tetramethylammonium chloride was added to the alcohol solution before it was titrated with HCl. The salt helped to eliminate noise encountered in the high-resistance alcohol solution and improved the separation of end points.

For the reactions using a 1:1 ratio of isocyanate/carbinol, plots of $1/(c - c_\infty)$ *vs.* time gave straight lines over a span of at least 2 half-lives. Second-order kinetics were followed from at least 4:1 to 1:4 isocyanate/carbinol ratios. For the reactions in which initial concentrations of isocyanate and carbinol were not similar, plots of log $[b(a - x)/a(b - x)]$ *vs.* time were linear. Duplicate runs were made for each reaction and the average rate constant is reported. The reactions were all carried out at 100 ± 0.1° in toluene solvent.

Synthesis of Carbinols. (4-Nitrophenyl)diphenylmethanol (VII).—A slurry of 30 g (0.093 mol) of (4-nitrophenyl)diphenylchloromethane in 600 ml of water, 600 ml of dioxane, and 60 ml of 70% $HClO_4$ was heated under reflux for 1 hr. The cooled mixture was poured into 5 l. of H_2O and stored at 0° overnight. The crude product weighed 29 g. Recrystallization from benzene–petroleum ether (bp 60–70°) gave 21.0 g (74.0%) of VII, mp 97.5–99° (lit.[5] mp 97–98°).

Bis(4-nitrophenyl)phenylmethanol (VIII).—Bis(4-nitrophenyl)chloromethane (13.8 g, 0.037 mol) was suspended in a mixture of 200 ml of H_2O, 200 ml of dioxane, and 20 ml of 70% $HClO_4$ and stirred and heated under reflux for 2.5 hr. The mixture was cooled, added to 4 l. of H_2O, and cooled at 0° overnight. The H_2O was decanted and the oil was washed with H_2O and then dissolved in 150 ml of warm toluene. Dilution with 150 ml of petroleum ether precipitated an oil which crystallized upon scratching, yield 10.4 g (80.0%), mp 137–138°. Recrystallization did not change the melting point.

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[1] Taken in part from the M. S. Thesis of D. J. T., DePauw University, 1967.

[2] J. W. McFarland, D. E. Lenz, and D. J. Grosse, *J. Org. Chem.*, **31**, 3798 (1966).

[3] J. W. McFarland D. E. Lenz, and D. J. Grosse, *ibid.*, **33**, 3514 (1968).

[4] J. W. McFarland, D. Green, and W. Hubble, *ibid.*, **35**, 702 (1970).

[5] P. D. Bartlett and J. D. Cotman, *J. Amer. Chem. Soc.*, **72**, 3095 (1950).