The Chemistry of Sulfonyl Isocyanates. IV. Kinetics of the Reaction with Triphenylmethanol

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Benzenesulfonyl isocyanate (I) was allowed to react with triphenylmethanol (II) to give N-(triphenylmethyl)-benzenesulfonamide (III) and carbon dioxide. The kinetics of the reaction were studied over a wide temperature and reagent ratio range. The reaction was found to be first order for both I and II when followed by either isocyanate disappearance or by carbon dioxide evolution. The isocyanate, however, disappeared two to three times faster than CO_2 was evolved. The visible spectrum of reaction solutions showed a buildup at 420 mμ of a species which slowly decreased during the latter stages of reaction. A tentative mechanism for the reaction is proposed.

It was shown earlier that sulfonyl isocyanates, when allowed to react with hindered phenols and alcohols, give normal urethan products.[2] It was also found that the sulfonyl isocyanates, when allowed to react with triphenylmethanol and many other triarylcarbinols, afford the corresponding N-(triarylmethyl)sulfonamides plus carbon dioxide.[3] Although the reactions of ordinary isocyanates, especially the reactions of phenyl isocyanate and alcohols, have been the object of many kinetic studies,[4-10] no kinetic studies have been made using sulfonyl isocyanates. The reactions of alcohols with phenyl isocyanate usually followed second-order kinetics and it has been suggested that the formation of an isocyanate–alcohol complex precedes the rate-determining step.

This paper records the results which we have obtained from the kinetic study of benzenesulfonyl isocyanate (I) in its reactions with triphenylmethanol (II). It was of interest to determine what effect the $-SO_2-$ group would have upon the reactivity of an adjacent -NCO group. The kinetic studies were carried out in two general ways. First, the reaction was followed by measuring the disappearance of isocyanate, Second, since carbon dioxide was one of the products, the rate of evolution of this gas was studied.

Experimental Section

Reagents.—Benzenesulfonyl isocyanate (I) was prepared by the method of Billeter[11] and purified by distilling through a 30-in. spinning-band column. Triphenylmethanol (II) was a commercial product. Toluene was reagent grade and was dried over sodium before use. The di-*n*-butylamine was Eastman White Label grade reagent.

Kinetics. A. Isocyanate Disappearance.—All-glass reaction vessels were washed with concentrated H_2SO_4, followed by water, and acetone. The vessels were dried for at least 1 hr at 110° and cooled under N_2 just prior to use. A solution of approximately 0.04 *N* di-*n*-butylamine in toluene was prepared and standardized with HCl solution (approximately 0.01 *N*) using a procedure similar to that below for the samples. The isocyanate and triphenylmethanol were weighed to the nearest 1.0 mg and placed separately in 50-ml volumetric flasks. To each of the flasks was added about 40 ml of dry toluene and then the flasks were immersed in an oil bath thermostated to ±0.1° and allowed to reach temperature equilibrium. More toluene was added to give a volume of 50 ml.

The two solutions were then rapidly mixed in a 100-ml volumetric or round-bottomed flask and the stopwatch was started. From the stoppered flask were withdrawn 2-ml samples at various times. The samples were added to 10-ml of standardized di-*n*-butylamine solution and allowed to stand for 5 min. The mixture was diluted with 100 ml of 95% ethanol and the excess amine titrated with standardized HCl solution using a magnetic stirrer, an automatic constant-rate buret, a glass electrode, and a Sargent Model SR automatic self-balancing potentiometric recorder with a Sargent Model LS meter as a dc preamplifier. Before and after each run, a blank of a 10-ml aliquot of di-*n*-butylamine solution was titrated with HCl solution. The difference between the blank titration and sample titration multiplied by the normality of acid gave the concentration of isocyanate in the sample. This was converted into moles per liter.

For the reactions using 1:1 ratio of isocyanate/carbinol, plots of $1/C-C_\infty$ *vs.* *t* gave straight lines over a span of at least 2 half-lives. The isocyanate was consumed in greater than 90% in most cases. Second-order kinetics were followed from at least 4:1 to 1:4 isocyanate/carbinol ratios. For the latter reactions plots of $\log [b(a - x)]/[a(b - x)]$ *vs.* time were linear. Duplicate runs were made for each ratio of isocyanate/carbinol 4:1, 2:1, 1:1, 1:2, and 1:4 at temperatures of 56, 70, 80, 90, and 100°. The energy of activation, E_a, was determined by plotting $\log k$ *vs.* $1/T$.

B. Carbon Dioxide Evolution.—The separate solutions of I and II were prepared as before. After coming to temperature equilibrium during about 30 min the solutions were mixed in a three-necked round-bottomed flask preheated in the constant-temperature bath and connected by means of a glass capillary tube to a gas buret. Before mixing the two solutions were saturated with dry CO_2. Wooden sticks placed in the solutions helped to avoid supersaturation with CO_2. The stopwatch was started during mixing and the solution was magnetically stirred. A volume reading was made immediately after stoppering the flask and extrapolation to zero time gave the initial volume. Volume readings were taken every 5–10 min until about 75% of the theoretical CO_2 had been evolved, then at longer intervals. 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. Therefore, in plotting, the calculated concentrations of isocyanate were used. The temperatures employed were 70, 80, 90, and 100°.

Isolation of Product.—The product, N-(triphenylmethyl)-benzenesulfonamide (III),[3] was isolated by cooling the reaction mixture at 0° for 1 hr and then filtering off the precipitate. Purification was effected by recrystallization from toluene. Dilution of the original filtrate with petroleum ether gave no significant amount of solid. Removal of solvent under reduced pressure gave a residue from which traces of benzenesulfonamide and benzophenone were isolated. The amounts of III and CO_2 obtained from a reaction usually corresponded within 3%. However, both of these were usually less (often by as much as 10%) than the amount of isocyanate consumed.

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(6) J. W. Baker and J. Gaunt, *ibid.*, **151**, 19 (1949).

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TABLE I

REACTION OF BENZENESULFONYL ISOCYANATE (I) WITH TRIPHENYLMETHANOL (II) AT DIFFERENT TEMPERATURES

	Temperature, °C				
	56	70	80	90	100
$k \times 10^2$ (l. mol^{-1} min^{-1})	4.2 ± 0.2	8.0 ± 0.2	10.6 ± 0.6	17.3 + 0.4	29.6 ± 0.6

TABLE II

EFFECT OF CONCENTRATION ON RATE CONSTANT

Temperature, °C					
80			100		
Isocyanate, mol/l.	Carbinol, mol/l.	$k \times 10^2$	Isocyanate, mol/l.	Carbinol, mol/l.	$k \times 10^2$
5.08×10^{-2}	5.08×10^{-2}	11.1	5.07×10^{-2}	5.07×10^{-2}	30.2
5.02×10^{-2}	20.08×10^{-2}	10.0	5.01×10^{-2}	20.04×10^{-2}	29.0
20.01×10^{-2}	5.00×10^{-2}	10.6	20.08×10^{-2}	5.02×10^{-2}	29.7

Results

Benzenesulfonyl isocyanate (I) reacted smoothly with triphenylmethanol (II) at temperatures from 56 to 100° (Table I), in contrast to phenyl isocyanate[12] which reacted very slowly. Whereas the half-life of I was found to be about 65 min at 100°, very little of phenyl isocyanate had disappeared after 500 min under similar conditions. The reaction of I and II showed over-all second-order kinetics for at least 2 half-lives when the reaction was followed by the kinetic method (see A of the Experimental Section, Figure 1, and Tables II and III). Following the first 5–10% of reactions using different ratios of reagents, and employing eq 1 for initial

$$n_A = \frac{\log (dx/dt)_1 - \log (dx/dt)_2}{\log A_1 - \log A_2} \qquad (1)$$

rates[13] [where n_A is the order in reagent A, $(dx/dt)_1$ 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 orders were found to be 1.0 ± 0.1 and 1.1 ± 0.1, respectively, in I and II.

TABLE III

RATE CONSTANTS FOR REACTION OF BENZENESULFONYL ISOCYANATE (I) WITH TRIPHENYLMETHANOL (II)

($k \times 10^2$ l. mol^{-1} min^{-1})

	Temperature, °C			
	70	80	90	100
Isocyanate disappearance	8.0	10.6	17.3	29.6
CO_2 evolution	3.8	5.0	6.5	11.2

An alternative method for following the reaction of I and II was by measuring CO_2 evolution. The reaction again obeyed over-all second-order kinetics from 70 to 100° and over a 4:1 to 1:4 ratio range. By varying the ratio of reagents and comparing initial rates and half-lives, the reaction was shown to be first order in each of I and II. As demonstrated in Figure 2, however, the rate of CO_2 evolution was slower than isocyanate consumption. For convenience of comparison CO_2 was converted into moles per liter. The second-order rate constants evaluated from such a treatment were considerably lower than those obtained by measuring isocyanate disappearance (Table III). At all temperatures studied the rate of isocyanate disappearance was two to three times greater than CO_2 evolution.

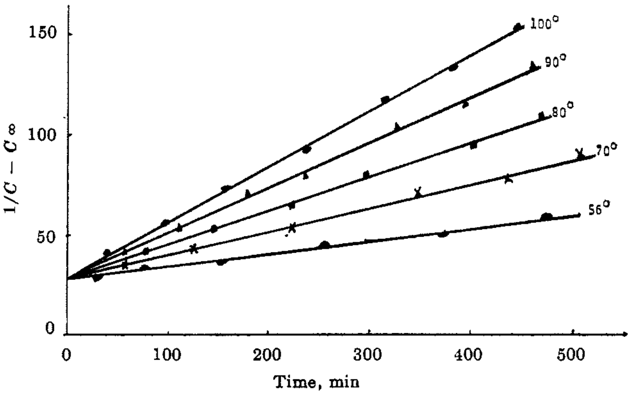

Figure 1.—Reaction of benzenesulfonyl isocyanate (I) and triphenylmethanol (II). (Approximately 5.0×10^{-2} M concentration of each.)

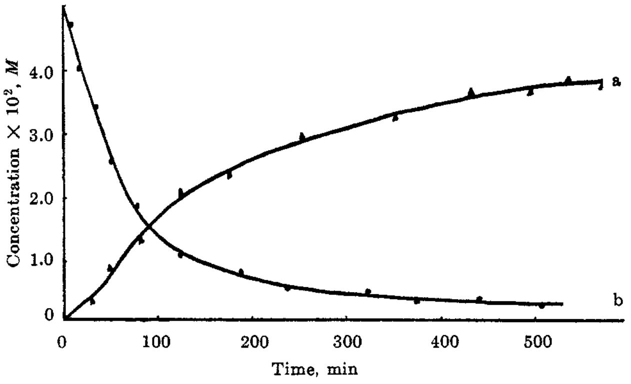

Figure 2.—Reaction of benzenesulfonyl isocyanate (I) and triphenylmethanol (II) at 100°: curve a, CO_2 evolution; curve b, isocyanate disappearance.

Various attempts were made to isolate products other than N-(triphenylmethyl)benzenesulfonamide (III). Only traces of benzenesulfonamide and benzophenone were isolated and it was not clear whether they were products from the reaction of I and II or were formed during work-up. The reaction was run at 0°, but again the main product was III accompanied by a trace of N,N′-dibenzenesulfonylurea in one case.

During the reaction of I and II the solution became yellow or orange. An inspection of the visible spectrum of the solution revealed an increasing absorption at 420 mμ during the early stages of the reaction and diminishing absorption during the latter stages. Attempts to obtain quantitative results from the absorptions have thus far been unsuccessful.

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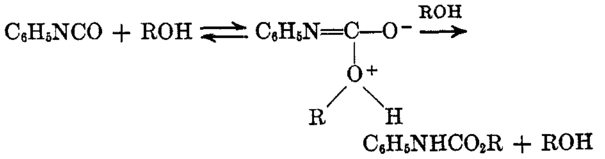
Discussion

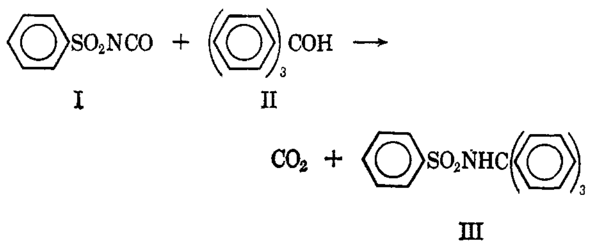
In their reactions with nucleophiles isocyanates should react faster if the NCO group is rendered more positive. Placing substituents on the rings of aromatic isocyanates has shown this to be true.[14,15] The sulfonyl group exhibits strong electronegative effects when adjacent to an NCO group as shown by the difference in reactivity of phenyl isocyanate and benzenesulfonyl isocyanate (I). Whatever steric effect the SO_2 may show toward adjacent nucleophilic attack[16] is greatly submerged by its opposite inductive effect.

It is interesting to note that the second-order rate constant obtained for the reaction is independent of the ratio of the two reagents over the range studied. Baker and Gaunt[6] had found that the apparent second-order rate constants for reactions of phenyl isocyanate and alcohols were dependent upon alcohol concentration. For that reason those workers proposed the mechanism given in reaction 2.



$$C_6H_5NCO + ROH \rightleftharpoons C_6H_5N{=}\underset{\underset{R\ \ \ H}{\overset{|}{O^+}}}{C}{-}O^- \xrightarrow{ROH} C_6H_5NHCO_2R + ROH \quad (2)$$

The fact that CO_2 evolution is slower than expected from the rate of isocyanate consumption could mean one of two things. (a) Carbon dioxide is only one of the products from the reaction of I and II, and 3 represents only one of the reactions that take place.



(3)

This factor may indeed contribute in a small way to the discrepancy since, as it was stated in the Experimental Section, the amount of CO_2 or III obtained often lagged behind the consumption of I by as much as 10%, but such a factor is far too small to account for the fact that I is consumed at two to three times the rate of CO_2 evolution.

(b) A species builds up in the reaction mixture which does not spontaneously decompose. Corroboration of this suggestion was obtained from the visible spectrum. When isocyanate and carbinol were mixed the reaction solution began to turn yellow or orange depending upon the temperature. The visible spectrum showed that the solution gradually increased in absorption at approximately 420 mμ to a maximum and then slowly decreased. A solution of II in sulfuric acid shows similar absorption[17] which has been attributed to triphenylmethylcarbonium ion; consequently, it is believed that triphenylmethylcarbonium ion or a similar species exists in solution. The initial very slow evolution of CO_2 (Figure 2) is consistent with this postulate.

Any mechanism proposed for the above reaction must be consistent with the following facts.

(1) The rate of isocyanate disappearance is greater than that of CO_2 evolution.

(2) The initial specific rate of CO_2 evolution is slower than the average specific rate.

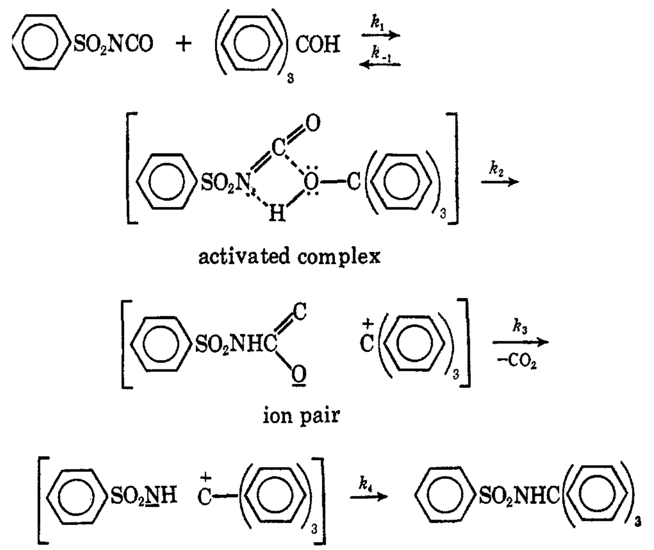
(3) The urethan could not be isolated even at low temperature.

(4) The visible spectrum suggests triphenylmethylcarbonium ion or similar species.

(5) The rate of isocyanate disappearance and the rate of CO_2 evolution are dependent upon the concentrations of I and II.

On the basis of the presently available experimental evidence, the tentative mechanism given in Scheme I is proposed for the reaction.

Scheme I



If the first reaction is a fast equilibrium, k_2 measures the rate of isocyanate disappearance. The faster rate of isocyanate consumption compared with CO_2 evolution is consistent with the above mechanism if $k_2 > k_3$. The mechanism is also consistent with the fact that k_3 determined during the early stages of the reaction was lower than the average. There would be little ion pair during the early stages of reaction and CO_2 evolution would lag until the concentration built up. Efforts are at present underway to obtain more mechanistic evidence, including study of the spectral behavior of reaction solutions.

Registry No.—I, 2845-62-7; II, 76-84-6.

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