TABLE IV *Continued*

Chelate	M.p. °C.	Sample wt., g.	Percentage, weight loss at 240–260° After 4 hr.	After 8 hr.	After 12 hr.	After 24 hr.	After 48 hr.	Remarks
Copper		0.4984	25.5	26.2	26.6	27.8		Became very dark, formed crust within 4 hr., appeared to be little but ash left after 8 hr.
Iron	145	1.8867	15.6	17.0	17.3	18.5		Was black, apparently decomposed within 8 hr.
Disalicylal triethylenetetraamine								
Zinc	235	3.6239						Sample decomposed and foamed out of vial within four hours

[a] 1,8(N)-3,6(S) is S,S′-bis-(2-aminoethyl)-ethanedithiol-1,2.

The more detailed thermal stability studies of the chelates of Schiff bases I, III and IV were carried out by heating accurately weighed samples of about 0.2 g. of the 12 chelates in open Pyrex sample vials, 45 × 13 mm., in a muffle furnace at 240–260° for periods of 4, 6, 8, 10, 12 and 24 hours. The samples were cooled in a desiccator, weighed, and the percentage weight losses calculated. The results are reported in the form of time–decomposition curves in Fig. 1. A sample of the Zn(II) chelate of Schiff base I was heated similarly for 168 hours after which the weight loss was 15.7%.

The stability of the chelates of Schiff base I under nitrogen were tested by heating accurately weighed samples of about 0.2 g. in Pyrex vials in a glass container which was evacuated and flushed with nitrogen several times, finally filled with nitrogen, then heated in a Woods metal-bath for 4 hours at approximately 250°. The percentage weight losses are given in Table V, along with the corresponding weight losses for samples heated open to atmosphere.

TABLE V

PERCENTAGE WEIGHT LOSSES OF THE CHELATES OF SCHIFF BASE I HEATED UNDER NITROGEN AND IN AIR

Metal	Weight loss under nitrogen, %	Weight loss in air, %
Zn(II)	0.00	1.72
Ni(II)	0.20	6.81
Cu(II)	4.93	4.73
Fe(II)	3.25	3.41

Acknowledgment.—We are indebted to Mr. J. J. Brader, Jr., for the infrared results and to Mr. J. Nemeth for the analyses.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MANITOBA AND THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Isotope Effect in the Hydrolysis of Triphenylsilane-*d*[1]

BY CARL BRYNKO, G. E. DUNN, HENRY GILMAN AND G. S. HAMMOND

RECEIVED JUNE 8, 1956

The rate ratio, k_H/k_D, for the hydrolysis of triphenylsilane and triphenylsilane-*d* in a mixture of toluene, piperidine and water has been found to be 1.41 by kinetic measurement of the rates of hydrolysis of the separate compounds, and 1.47 by allowing the two compounds to compete in the same solution. These results agree qualitatively with those obtained by Wilzbach and Kaplan under slightly different conditions and show that the abnormal isotope effect reported earlier[2] was erroneous.

In 1951, three of the authors reported some preliminary results of an investigation into the mechanism of hydrolysis of triphenylsilane in moist piperidine[2].

$$(C_6H_5)_3SiH + H_2O \xrightarrow{\text{base}} (C_6H_5)_3SiOH + H_2$$

Separate kinetic measurements of the rates of hydrolysis of triphenylsilane and triphenylsilane-*d* indicated that the deuterium compound hydrolyzed almost six times faster than its protium analog. Such an unusual isotope effect required confirmation, and this paper records a repetition of the kinetic measurements on new samples of triphenylsilane and triphenylsilane-*d* together with experiments in which the two isotopic forms were subjected to competitive hydrolysis in one solution. The rate-ratio, k_H/k_D, was found to be 1.41 by the kinetic method and 1.47 by the competition experiments.

Before the completion of this work Wilzbach and Kaplan reported the results of similar experiments using tritium-substituted silanes,[3] and later they extended their work to include triphenylsilane-*d*.[4] Using a competition method, they found the rate-ratios for isotopically substituted triphenylsilanes to be: $k_H/k_T = 1.26$ and $k_H/k_D = 1.15$. In view of the differences in methods of hydrolysis and analysis the discrepancy between our values and these is probably not significant. Consequently, our results confirm those of Wilzbach and Kaplan and both show that the previously-reported abnormal isotope effect was erroneous.

Further investigation and discussion of the mechanism of hydrolysis of triphenylsilane in moist piperidine will be reported in a subsequent paper.

Experimental

Triphenylsilane and Triphenylsilane-*d*.—These compounds were prepared by reduction of commercial triphenylchlorosilane (Anderson Laboratories, Inc., Weston, Mich.) with lithium aluminum hydride and lithium aluminum deuteride, respectively, using the method previously described.[5] Yields of 60–64% of triphenylsilane and triphenylsilane-*d* were obtained, both melting at 44.0–44.5° (uncor.). Complete hydrolysis of the deuterated silane and analysis of its

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(1) Taken from the M.Sc. Thesis of Carl Brynko, the University of Manitoba, May, 1954. Inquiries concerning this paper should be addressed to G. E. Dunn, Chemistry Department, University of Manitoba, Winnipeg, Canada.

(2) H. Gilman, G. E. Dunn and G. S. Hammond, THIS JOURNAL, **73**, 4499 (1951).

(3) K. E. Wilzbach and L. Kaplan, *ibid.*, **74**, 6152 (1952).

(4) L. Kaplan and K. E. Wilzbach, *ibid.*, **77**, 1297 (1955).

(5) H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).

hydrogen by the method described below showed that it contained 91.8 mole-% triphenylsilane-*d*.

Melting point was found to be a very poor criterion of purity for these compounds. Some batches of triphenylchlorosilane gave triphenylsilane which hydrolyzed as much as ten times faster than similar preparations with the same melting point made from other batches of triphenylchlorosilane. Repeated recrystallization of the "fast" samples from petroleum ether (b.p. 60–80°) brought their rates of hydrolysis down to the "slow" figure without changing their melting points. Consequently, the minimum rate of hydrolysis was taken as the standard of purity for these compounds. Undoubtedly, the erronous isotope effect in our preliminary report resulted from insufficient attention to this point. Impurities isolated from typical preparations of triphenylsilane were triphenylsilanol, hexaphenyldisiloxane, hexaphenyldisilane and terphenyl, but none of these compounds when added to "slow" samples of triphenylsilane affected the rate of hydrolysis appreciably, even when they were present in much larger proportions than ever occurs naturally in a preparation of triphenylsilane. Attempts to isolate the impurities causing the accelerated rates were not pursued further.

Competitive Measurement of Rate Ratios.—Competitive hydrolyses were carried out in a Hempel gas buret over mercury. This unusual reaction vessel had the advantage that the amount of gas produced at any time could be conveniently observed and almost instantly isolated by simply raising the mercury with the reaction mixture on top of it and thus forcing the gas into a second container. The buret was surrounded by a glass jacket through which water was circulated from a thermostat maintained at 25.00 ± 0.01°. One outlet of the three-way stopcock at the top of the buret was connected to a separatory funnel through which the reactants could be added; the other outlet was connected to a storage gas buret. The whole apparatus was mounted on a ring-stand to which was clamped a stirring motor having on its chuck a large rubber stopper mounted off-center. Operation of the stirring motor during the reaction produced enough vibration of the whole apparatus to give the agitation which has been found necessary for smooth hydrogen evolution.[5,6]

A typical competitive hydrolysis was carried out as follows. The apparatus was brought to thermostat temperature, the mercury in the gas buret was raised to the stopcock, and the stopcock was closed. Weighed half-gram samples of triphenylsilane and triphenylsilane-*d* were dissolved in 20 ml. of sodium-dried toluene in the separatory funnel and to this was added a solution of 1.986 g. of water (0.110 mole) in 34.57 g. of piperidine (0.406 mole). (The piperidine had been dried over KOH and fractionated through a 15-plate column.) The two solutions were mixed quickly and drawn into the reaction buret by lowering the mercury. The mercury was raised so that the reaction mixture rose to the stopcock, thus excluding air, and the stopcock was closed. The stirring motor was started and the mercury levels were adjusted so as to maintain the gas produced in the reaction at atmospheric pressure. When approximately half the theoretical amount of hydrogen had been collected, the stopcock was turned to connect the reaction buret with the storage buret and the mercury levels were manipulated so as to transfer the hydrogen quickly and quantitatively to the storage buret. This hydrogen was freed from solvent vapors by passing it repeatedly through a Dry Ice trap, and the volume of the dry hydrogen was measured in order to calculate the percentage completion of the reaction. It was then analyzed for deuterium by the method described below.

The rate-ratio, k_H/k_D, was calculated from the data by the following method. The reaction has been shown to be first order with respect to triphenylsilane,[5] and all other reagents were used in excess so that the ratio of the rates of hydrolysis of triphenylsilane, k_H, and of triphenylsilane-*d*, k_D, is given by the expression

$$\frac{k_H}{k_D} = \log\frac{a}{a-x}\bigg/\log\frac{a'}{a'-x'}$$

where a is the initial concentration of triphenylsilane; $a - x$ is its concentration at some time, t; and a' and $a' - x'$ are the corresponding quantities for triphenylsilane-*d*. If $a'/a = A$, the ratio of D to H in the initial triphenylsilane; $x'/x = X$, the ratio of D to H in the product hydrogen; and $(x + x')/(a + a') = P$, the fraction of triphenylsilane reacted, then the above expression becomes

$$\frac{k_H}{k_D} = \frac{\log(1 + X) - \log[(1 + X) - P(1 + A)]}{\log(1 + 1/X) - \log[(1 + 1/X) - P(1 + 1/A)]}$$

The data and results calculated using this equation are shown in Table I.

TABLE I

RATE–RATIO, k_H/k_D, FROM COMPETITIVE RUNS

Quantity	Run 1	Run 2
Triphenylsilane, mole	0.003838	0.003838
Toluene, mole	.1874	.1874
Piperidine, mole	.4060	.4060
Water, mole	.1102	.1102
Mole-ratio D/H in triphenylsilane, (A)	.842 ± 0.001	.842 ± 0.001
Mole-ratio D/H in hydrogen, (X)	.630 ± .006	.621 ± .006
Fraction of triphenylsilane reacted, (P)	.456 ± .018	.412 ± .016
Rate-ratio, k_H/k_D	1.49 ± .04	1.47 ± .04

Deuterium Analysis of Hydrogen Gas.—The hydrogen obtained from a hydrolysis was diluted with dry hydrogen from a cylinder to a total volume of 600 ml. and oxidized to water by sweeping it with nitrogen over copper oxide at 370° in a Vycor combustion tube. The water produced (about 0.4 g.) was caught in a Dry Ice trap and purified by refluxing it over a mixture of potassium permanganate and calcium oxide and then distilling it according to the directions of Keston, Rittenberg and Schoenheimer.[7] The deuterium content of this water was determined by the density gradient tube method described by Anfinsen.[8]

Kinetic Measurement of Rate Ratios.—Kinetic runs were carried out in the same apparatus described above for competitive runs, except that the storage buret was replaced by a small Nujol-filled manometer which was used for accurate equalization of inside and outside pressures. When the apparatus had reached thermostat temperature (25°) a half-gram sample of triphenylsilane (or triphenylsilane-*d*) was dissolved in 10 ml. of toluene in the separatory funnel, and 20 ml. of a piperidine–water solution was added. The two solutions were mixed and quickly drawn into the reaction buret; the stopcock was closed and the stirring motor started. The volume of gas produced at atmospheric pressure was read from time to time during the reaction (V) and when it was complete (V_∞). At the end of the reaction the gas was passed back and forth through a Dry Ice trap until its volume was no longer changed; the decrease in volume (8.3%) was taken to be the volume of the solvent vapors contained in the gas, and this fraction was subtracted from each of the volume readings taken during the run. The total volume of dry gas was always

TABLE II

RATE-RATIO, k_H/k_D, FROM KINETIC RUNS

In each run 0.00192 mole of silicon compound was dissolved in a solution containing 0.0937 mole of toluene, 0.0551 mole of water and 0.203 mole of piperidine.

	$k \times 10^4$ sec.$^{-1}$, triphenylsilane	$k \times 10^4$ sec.$^{-1}$ triphenylsilane-*d*
Run 1	1.29 ± 0.05	0.910 ± 0.010
Run 2	1.27 ± .08	.905 ± .040
Run 3	1.27 ± .08	
Mean	1.28 ± 0.08	0.908 ± 0.040
k_H/k_D, mean	1.41 ± 0.15	

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(6) F. P. Price, THIS JOURNAL, **69**, 2600 (1947).

(7) A. S. Keston, D. Rittenberg and R. Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1937).

(8) C. Anfinsen in O. W. Wilson, A. O. C. Nier and S. P. Reimann "Preparation and Measurement of Isotropic Tracers," J. W. Edwards, Ann Arbor, Mich., 1948, pp. 61–67.

within 2% of the theoretical volume calculated from the weight of triphenylsilane. Pseudo-first-order rate constants were calculated from the usual plots of log $(V_\infty - V)$ against time and they agreed, within experimental error, with rate constants obtained using the more conventional apparatus described in an earlier paper.[5] The results are shown in Table II.

Acknowledgment.—The authors are grateful to the National Research Council of Canada for financial support of this research and for the gift of the lithium aluminum deuteride used in it.

WINNIPEG, MANITOBA
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[CONTRIBUTION NO. 204 FROM THE JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND COMPANY]

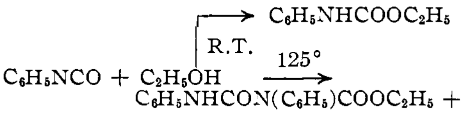
New Reactions of Phenyl Isocyanate and Ethyl Alcohol[1]

BY I. C. KOGON

RECEIVED MARCH 2, 1956

Phenyl isocyanate reacts with ethyl alcohol at 125° to give a 22.9% yield of ethyl α,γ-diphenylallophanate and a trace of phenyl isocyanate dimer. When N-methylmorpholine is added as a catalyst, the reaction is altered and the product is triphenylisocyanurate (isocyanate trimer) in excellent yield. Phenyl isocyanate without the ethyl alcohol and heated under the same conditions in the presence of N-methylmorpholine yields only a small quantity of phenyl isocyanate dimer. Evidence is presented supporting ethyl α,γ-diphenylallophanate and phenyl isocyanate dimer as intermediates that lead to the formation of triphenylisocyanurate.

It has been known for many years that ethyl carbanilate is formed when phenyl isocyanate reacts with ethyl alcohol at room temperature.[2] We have now found that when the temperature is elevated to 125° the product is ethyl α,γ-diphenylallophanate (I) and a small quantity of phenyl isocyanate dimer II.[3]



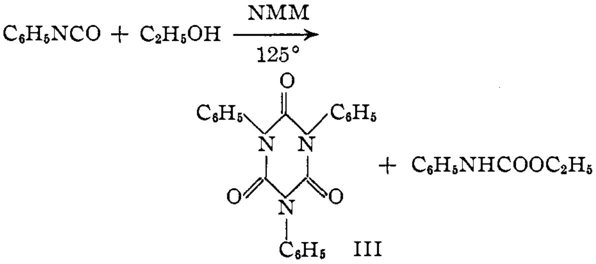
$$C_6H_5NCO + C_2H_5OH \xrightarrow{\text{R.T.}} C_6H_5NHCOOC_2H_5$$

$$C_6H_5NCO + C_2H_5OH \xrightarrow{125°} \underset{\text{I}}{C_6H_5NHCON(C_6H_5)COOC_2H_5} + \underset{\text{II}}{(C_6H_5NCO)_2}$$

Lakra and Dains[4] carried out a similar reaction at 150°, but they did not isolate I; their only product was a small quantity of carbanilide. The formation of the carbanilide was probably due to traces of moisture present in the reaction mixture.

Ethyl carbanilate also reacts with phenyl isocyanate to give I and II and is probably an intermediate for this reaction. In order to understand further this reaction a study was made of the effect of substituents on the reactivity of ethyl carbanilate and phenyl isocyanate (Table I). Electron-donating groups in the aromatic ring of the carbanilate and electron-withdrawing groups in phenyl isocyanate appeared to aid the reaction. An unexpected result was the relatively high yield of product obtained when phenyl isocyanate was treated with ethyl *p*-chlorocarbanilate.

When N-methylmorpholine (NMM) was used as a catalyst for the reaction of phenyl isocyanate and ethyl alcohol, the reaction was altered and triphenylisocyanurate (III) was obtained in excellent yield. Ethyl alcohol could again be replaced by ethyl carbanilate to give the same product.



III

The reaction was extended to include substituted aromatic isocyanates and substituted ethyl carbanilates. The results are summarized in Table II. In order to demonstrate that only the initial aryl isocyanate and none of the carbanilate enters into the formation of triarylisocyanurate, the following mixtures were heated in the presence of a catalytic quantity of NMM: (a) phenyl isocyanate and ethyl *p*-chlorocarbanilate, (b) *p*-tolyl isocyanate and ethyl carbanilate, (c) *o*-chlorophenyl isocyanate and ethyl *m*-chlorocarbanilate. The major product isolated in each case was the triarylisocyanurate of the initial aryl isocyanate present. The yield of product from these reactions was lower than the yield of product from the experiments in which the aryl isocyanate and the substituted ethyl carbanilates had the same substitution on the aromatic ring. This lower yield from reactions a, b and c is probably due to an exchange reaction between the aryl isocyanate and the substituted ethyl carbanilate.[5] No trimeric product was isolated from a mixture of phenyl isocyanate, ethyl N-methyl carbanilate and NMM heated at 125° for 24 hours. The hydrogen atom present on the nitrogen of ethyl carbanilate therefore must be important in the formation of III. Phenyl isocyanate gives III when heated with a small quantity of a basic inorganic salt.[6-9] We have trimerized a number of aryl iso-

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[1] Presented before the section on Organic Chemistry, Eighth Annual Delaware Chemical Symposium at Newark, Delaware, February 1956.

[2] (a) R. L. Shriner and R. C. Fuson, "Identification of Pure Organic Compounds," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 136; (b) C. Naegali, A. Tyaliji, L. Conrad and F. Litwan, *Helv. Chim. Acta*, **21**, 1100, 1127 (1938); (c) D. S. Tarbell, R. C. Mallatt and J. W. Wilson, THIS JOURNAL, **64**, 2229 (1942); (d) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947).

[3] A. W. Hofmann, *Ber.*, **4**, 247 (1871). The infrared spectrum and melting point of I were identical with those of the product obtained from Hofmann's procedure.

[4] H. Lakra and F. B. Dains, THIS JOURNAL, **51**, 2220 (1929).

[5] E. J. Goldberg, private communication.

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[8] J. Blair and G. Smith, THIS JOURNAL, **56**, 907 (1934).

[9] H. Staudinger, "Die Ketene," Enke, Stuttgart, 1912, pp. 126-127.