values. However, the deviations from experimental values are sufficiently small to warrant the use of the method for many chemical engineering process calculations for which reliable data over a range are not available. As an example, the expansion factor[7] of Watson's correlations is closely related to the compressibilities measured in this investigation. In Fig. 2 are plotted values of W for various reduced conditions of pressure and temperature, using the data[8] of 2,2,4-trimethylpentane as the reference liquid. Using this chart, values of the expansion factor W for a liquid of unknown density may be then evaluated by means of the relation ρ (density of unknown) = $(\rho_1/W_1)W$, where ρ_1 and W_1 are single, experimental values of the liquid density and the expansion factor for the unknown liquid. Table IV gives a comparison of experimental and calculated density values for hexamethylethane; the agreement is satisfactory enough for many engineering calculations.

The accuracy of the observed compressibility data of this investigation on 2,2,3,3-tetramethylbutane is the same as that claimed[8] for 2,2,4-trimethylpentane, *viz.*, 0.2%.

Acknowledgment.—The authors wish to thank Dr. George Calingaert of the Ethyl Gasoline Corporation for the donation of the samples of hexamethylethane used in this investigation.

Summary

1. The compressibility of highly purified 2,2,-3,3-tetramethylbutane has been determined from 110 to 270° at pressures ranging from approximately 5 to 300 atmospheres.

2. The pressures at the solid–liquid transition were determined at three temperatures, 110, 120 and 130°.

3. The method of correlating liquid densities, as proposed by Watson, has been applied to the data of this investigation and the results were quite satisfactory.

AUSTIN, TEXAS RECEIVED MARCH 17, 1947

[7] $\rho(\text{density}) = \dfrac{PM}{ZRT} = \dfrac{P_R}{ZRT}\,\dfrac{P_cM}{T_c} = W\,\dfrac{P_cM}{T_c}.$

[8] Felsing and Watson, THIS JOURNAL, **65**, 780 (1943).

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Ionization of Ethyl Nitrate in Sulfuric Acid

BY LESTER P. KUHN

As part of our program for studying the chemistry of nitrate esters, we have investigated the behavior of ethyl nitrate in sulfuric acid. We have found interesting similarities between this system and the system nitric acid or nitric anhydride–sulfuric acid. A knowledge of these systems is essential for understanding the mechanism of nitration with mixed acids. Because of the current interest evinced in this problem by recent publications[1,2,3] we are publishing our results at this time. These recent papers give convincing evidence that nitric acid and nitric anhydride yield NO_2^+ ions in sulfuric acid. On the basis of spectroscopic and cryoscopic evidence and chemical reactivity, it can be shown that ethyl nitrate also yields NO_2^+ ions in sulfuric acid.

Spectroscopic Evidence.—Like nitric acid, ethyl nitrate shows an ultraviolet absorption spectrum in sulfuric acid which is different from that of its solution in an inert solvent such as chloroform as shown in Fig. 1. Furthermore, the spectra of sulfuric acid solutions of ethyl nitrate and nitric acid are almost identical.

Cryoscopic Evidence.—From freezing point depression measurements of the sulfuric acid solutions we have obtained "*i*" values of 3.97 for nitric acid, 4.95 for ethyl nitrate, and 5.50 for nitric anhydride. The "*i*" value tells how many particles are obtained from each molecule of solute. Our values are in good agreement with those obtained by Ingold and co-workers, 3.82 for nitric acid and 5.85 for nitric anhydride, which appeared in the literature[3] after our measurements were made. Hantzsch,[4] in his classical work on solutions in sulfuric acid, obtained "*i*" values of 2–3 for nitric acid and 3–4 for ethyl nitrate. As explained by Hammett,[5] the sulfuric acid for freezing point depression measurements must contain a small amount of water to yield the proper "*i*" values. Since Hantzsch used 100% sulfuric acid it is to be expected that his values be low.

Most organic acids and esters act like bases in sulfuric acid and ionize according to the equation

$$RCOOR' + H_2SO_4 = RCOOR'H^+ + HSO_4^-$$

giving an "*i*" value of 2. The high "*i*" values of nitric acid and its ester are strongly reminiscent of the complex ionization which Treffers and Hammett[6] discovered to be exhibited by certain sterically hindered aromatic acids such as mesitoic acid and its esters which have "*i*" values of 4 and 5, respectively. The complex ionization is be-

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[1] Bennett, Brand and Williams, *J. Chem. Soc.*, 869, 875, 880 (1946).

[2] Westheimer and Kharasch, THIS JOURNAL, **68**, 1871 (1946).

[3] Ingold, *et al.*, *Nature*, **158**, 448, 480 (1946).

[4] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); **62**, 626 (1907); **65**, 40 (1908).

[5] Hammett, "Physical Organic Chemistry," McGraw-Hill, Book Co., New York, N. Y., 1940.

[6] Treffers and Hammett, THIS JOURNAL, **59**, 1708 (1937).

lieved to proceed according to the following reactions[7]

$$RCOOH + H_2SO_4 = RCOOHH^+ + HSO_4^- \quad (1)$$
$$RCOOHH^+ = RCO^+ + H_2O \quad (2)$$
$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \quad (3)$$
$$\overline{RCOOH + 2H_2SO_4 = RCO^+ + H_3O^+ + 2HSO_4^-} \text{ (over-all reaction).}$$

In the case of the ester, step 3 is replaced by the equation

$$ROH + 2H_2SO_4 = ROSO_3H + H_3O^+ + HSO_4^-$$

which accounts for its "*i*" value of 5 as compared with 4 for the free acid.

The "*i*" values of nitric acid and its derivatives indicate that they ionize in a similar fashion as shown below. Nitric acid and ethyl nitrate

$$RONO_2 + H_2SO_4 = \overset{H}{RONO_2}{}^+ + HSO_4^-$$
$$\overset{H}{RONO_2}{}^+ = ROH + NO_2^+$$
$$ROH + 2H_2SO_4 = ROSO_3H + H_3O^+ + HSO_4^-$$

Nitric anhydride

$$(O_2N)_2O + H_2SO_4 = (O_2N)_2OH^+ + HSO_4^-$$
$$(O_2N)_2OH^+ = NO_2^+ = HONO_2^+$$
$$HONO_2 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

The tendency of nitric acid and its derivatives to show complex ionization is due to the considerable amount of resonance stabilization to be expected of the NO_2^+ ion as indicated by the following possible structures which can be drawn

$$:\overset{+}{\ddot{O}}-\ddot{N}=\ddot{O}: \qquad :\ddot{O}=\overset{+}{N}=\ddot{O}: \qquad :\ddot{O}=\ddot{N}-\ddot{O}:^{+}$$

Evidence Based upon Chemical Reactivity.—Hammett and Treffers[6] have shown that a criterion for complex ionization is the fact that when an ester which exhibits complex ionization is dissolved in sulfuric acid and the sulfuric acid solution is poured into ice water the corresponding acid is obtained, whereas esters which ionize normally are recovered unchanged when subjected to the same treatment. Similarly, as demonstrated by Newman,[8] an acid which undergoes complex ionization is converted into its ester when its sulfuric acid solution is poured into cold alcohol, whereas an acid which ionizes normally is recovered unchanged. Both ethyl nitrate and nitric acid give positive tests for complex ionization. A solution of ethyl nitrate in cold 100% sulfuric acid was poured into ice water. The resulting solution which was perfectly clear and had no ethyl nitrate layer gave the ultraviolet absorption curve of a dilute solution of nitric acid (nitrate ion). To prove that hydrolysis had not taken place after the sulfuric acid solution had been poured into the ice water, ethyl nitrate was mixed with cold water and pure sulfuric acid was added to the mixture. Ethyl nitrate remained as a separate layer and the aqueous solution gave an absorption curve which indicated the absence of nitrate ions and the presence of unhydrolyzed ethyl nitrate. Ethyl nitrate would not be expected to hydrolyze under these conditions for it is known that it hydrolyzes very slowly in aqueous acid.[9] By pouring a sulfuric acid solution of nitric acid into cold absolute ethanol, ethyl nitrate was obtained. It was identified by its boiling point and density.

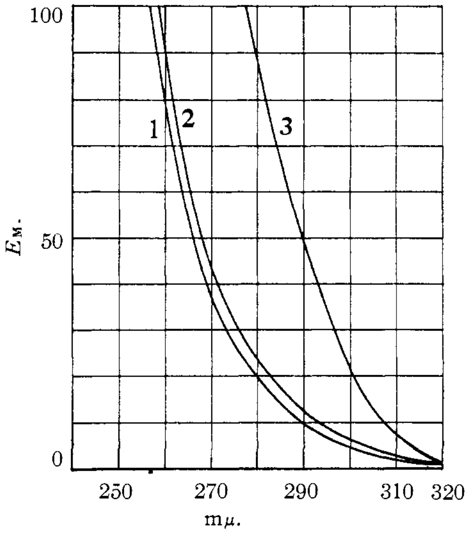

Fig. 1.—(1) KNO_3 in H_2SO_4, 1.26 g./100 ml.; (2) $EtONO_2$ in H_2SO_4, 1.20 g./100 ml.; (3) $EtONO_2$ in $CHCl_3$, 1.20 g./100 ml.

These results are in harmony with the generally accepted theory of mixed acid nitration in which the first step is considered to be the rapid formation of NO_2^+ ions and these are the active nitrating agent. The replacement of nitric acid with ethyl nitrate should not affect the nitration rate. Although no kinetic data are available it has been shown that mixtures of ethyl nitrate and sulfuric acid are powerful nitrating agents.[10]

Experimental

Spectrophotometric Measurements.—A Beckman spectrophotometer was used with 1-cm. quartz absorption cells.

Cryoscopic Measurements.—The apparatus and method was essentially that of Newman, *et al.*[11]

Hydrolysis Experiments.—One gram of ethyl nitrate was dissolved in 5 ml. of 100% sulfuric acid and poured into ice water. The solution was diluted to 100 ml. and its absorption spectrum was measured. It was the same as that of a dilute solution of nitric acid. In another experiment ethyl nitrate was mixed with ice water and 5 ml. of 100% sulfuric acid was added. A lower layer of ethyl nitrate formed and the absorption spectrum of the aqueous portion was that of undissociated ethyl nitrate, not of nitrate ions. Three ml. of 100% nitric acid was dissolved in 10 ml. of 100% sulfuric acid and the solution was added slowly with stirring to 30 ml. of absolute ethanol which contained several pieces of Dry Ice to keep the temperature below 0°. The resulting solution was poured into water and a lower layer of ethyl nitrate formed which was drawn off, dried over sodium sulfate and distilled, b. p. 87–88°, d^4_{25} 1.100.

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[7] Day and Ingold, *Trans. Faraday Soc.*, **37**, 698 (1941).

[8] Newman, THIS JOURNAL, **63**, 2431 (1941).

[9] Olivier and Berger, *Rec. trav. chim.*, **41**, 637 (1922).

[10] Raudnitz, *Ber.*, **60**, 738 (1927).

[11] Newman, Kuivila and Garrett, THIS JOURNAL, **67**, 704 (1945).

Summary

Evidence based upon cryoscopic and spectroscopic data is presented showing that ethyl nitrate yields NO_2^+ ions in sulfuric acid. It is suggested that this ester exhibits the same complex ionization which, as Hammett found, is shown by certain sterically hindered benzoic acids. Hydrolysis and esterification experiments confirm this belief.

ABERDEEN PROVING GROUND, MD.

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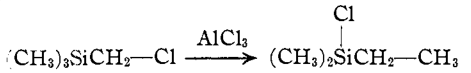
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Intramolecular Rearrangement of Chloromethyltrimethylsilane[1]

BY FRANK C. WHITMORE, LEO H. SOMMER AND JACK GOLD

Reactions of neopentyl compounds which deprive the neopentyl group of its electron pair result in rearranged products containing the *t*-amyl group.[2]

The present paper reports an analogous reaction of silico-neopentyl chloride (chloromethyltrimethylsilane) with aluminum chloride to give ethyldimethylchlorosilane. This is the first intramolecular rearrangement in an organosilicon compound.



$$(CH_3)_3SiCH_2—Cl \xrightarrow{AlCl_3} (CH_3)_2\overset{Cl}{Si}CH_2—CH_3$$

Experimental

Chloromethyltrimethylsilane.—This chloride[3] was prepared in 90% yield from chloromethyldimethylchlorosilane[4] and methylmagnesium bromide.[5]

Rearrangement of the Chloride.—In a 500-cc. round-bottomed flask fitted with a reflux condenser, thermometer in liquid, and a sulfuric acid trap, there were placed 184 g. (1.5 moles) of the chloride and 2 g. of powdered anhydrous aluminum chloride. Heating of the reaction mixture to 85° with a small flame initiated a *vigorous exothermal reaction*, which continued spontaneously for one-half hour after removal of the flame. It was necessary to cool the reaction flask intermittently in order to prevent loss of material through the condenser. At the end of this reaction the liquid temperature was 90° with little reflux. No loss in weight occurred during the reaction.

After cooling, a sample of the clear supernatant liquid was withdrawn, dissolved in isopropyl alcohol and titrated with 0.5 *N* sodium hydroxide. The calculated neutral equivalent for complete rearrangement of chlorine from carbon to silicon is 122.6. The value obtained, 155, indicated about 79% rearrangement. Silico-neopentyl chloride does not react with dilute alkali under these conditions.[3]

The reaction product was then flash distilled under reduced pressure. The distillate was fractionated at 734 mm. through a column of 12 theoretical plates to give fractions of the indicated boiling ranges and weights (g.): I, 57–89°, 13.2; II, 89–92.2°, 98; III, 92.2–98.5°, 18.2; IV, 98.5–113°, 5; res. 7.0.

Fraction II represents a 53% yield of slightly impure ethyldimethylchlorosilane containing a small amount of unchanged chloromethyltrimethylsilane. Since a total chlorine analysis or a silicon analysis would not distinguish these isomers, the product was analyzed in the usual way for chlorine attached to silicon.

Anal. Calcd. for $C_4H_{11}SiCl$: Cl, 29.0. Found: 27.5.

The identity of the product was confirmed by its action with methylmagnesium bromide to give the known ethyltrimethylsilane,[6] in 73% yield, b. p. 62.7–63.2° at 736 mm., $n^{20}D$ 1.3820, d^{20} 0.6842. Since the submission of this paper, the rearranged chloride has been prepared from dimethyldichlorosilane and ethylmagnesium bromide.[7]

The components of the reaction product boiling outside the range of ethyldimethylchlorosilane and silico-neopentyl chloride, 89–97°, are due to a partial redistribution of the ethyldimethylchlorosilane by aluminum chloride to give trimethylchlorosilane (b. p. 57°) and diethylmethylchlorosilane (b. p. 119°). The analogous ethyldimethyllead chloride gives the four R_3PbCl compounds in a random equilibrium mixture, as does also a mixture of trimethyl- and triethyllead chlorides.[8] In order to check the redistribution of trialkylchlorosilanes, a mixture of trimethylchlorosilane, 43.5 g. (0.4 mole), triethylchlorosilane, 60 g. (0.4 mole), and 2.0 g. of powdered aluminum chloride was refluxed for four hours. After flash distillation under vacuum, fractionation at 734 mm. of the 99 g. distillate gave 4 g. of impure trimethylchlorosilane, b. p. 57–60°; 25.7 g. (0.21 mole) of ethyldimethylchlorosilane, b. p. 89–90.5°, neut. equiv. 121.5; 35.8 g. (0.26 mole) of diethylmethylchlorosilane, b. p. 119–120°, neut. equiv. 137.2 (calcd., 136.5); and 5.5 g. (0.03 mole) of triethylchlorosilane, b. p. 144°.

In comparison experiments, neopentyl chloride[9] behaved very differently from chloromethyltrimethylsilane. The former was practically unchanged by a small proportion of anhydrous aluminum chloride. A proportion of 15 g. of chloride to 2 g. of aluminum chloride gave more complete reaction. Hydrogen chloride was evolved at room temperature. No appreciable heat was noted. Less than 0.5 cc. of liquid condensed in a Dry Ice trap. This did not decolorize bromine in carbon tetrachloride. When action had ceased, the mixture was treated with sodium carbonate solution. The organic layer was separated and distilled to give 4 g. of material boiling 65–220° and 3 g. of residue. The products were unchanged chloride and polyisoamylenes.

Discussion

Chloromethyltrimethylsilane, like neopentyl chloride,[9] can be distilled at atmospheric pressure and undergoes no change on long standing. In the preparation of the former by the photochemical chlorination of tetramethylsilane, no ethyldi-

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[1] Paper 9 in a series on molecular rearrangements. For Paper 8 see Whitmore and Carney, THIS JOURNAL, **63**, 2633 (1941). Also Paper 9 in a series on organosilicon compounds. For paper 8 see Sommer, Pietrusza and Whitmore, *ibid.*, **68**, 2282 (1946).

[2] (a) Whitmore and Rothrock, *ibid.*, **54**, 3431 (1934); (b) Whitmore and Fleming, *J. Chem. Soc.*, 1269 (1934); (c) Whitmore, Wittle and Popkin, THIS JOURNAL, **61**, 1586 (1939).

[3] Whitmore and Sommer, *ibid.*, **68**, 481 (1946).

[4] Krieble and Elliott, *ibid.*, **67**, 1810 (1945).

[5] For a similar synthesis of α-chloroethyltrimethylsilane see Sommer and Whitmore, *ibid.*, **68**, 485 (1946).

[6] Whitmore, Sommer, DiGiorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, *ibid.*, **68**, 475 (1946).

[7] Lewis, *ibid.*, **69**, 717 (1947).

[8] Calingaert, *et al.*, *ibid.*, **62**, 1104 (1940).

[9] Fleming and Whitmore, *ibid.*, **54**, 3460 (1932).