tion behavior of proteins depended on the specific acid or base used. Katchalsky[3] noted a difference in the viscosity behavior of polyacrylic acid neutralized with NaOH and KOH, respectively. It is reasonable to assume that these differences are caused by the extremely close associations of the gegenions with the polymer chain, due to the very high potential on the chain. A consequence of this might be that the effect would depend strongly on the size of the gegenion.

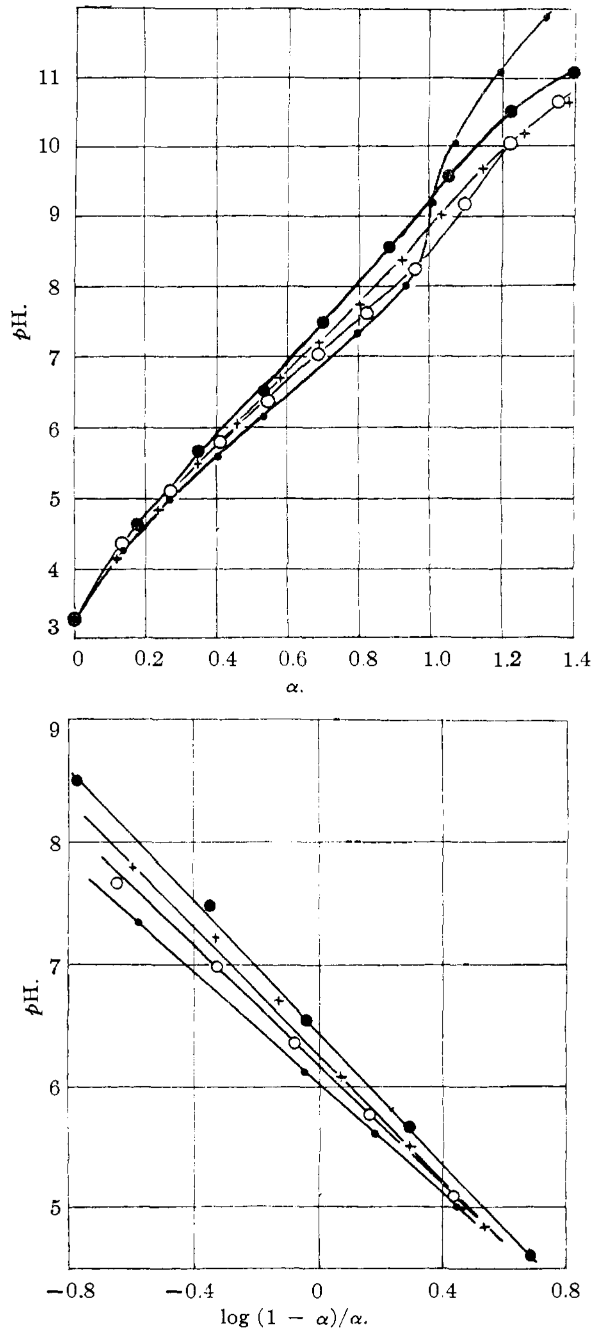

Fig. 1a and 1b.—Titration of 0.0128 N polyacrylic acid with: potassium hydroxide (•); tetramethylammonium hydroxide (O); tetraethylammonium hydroxide (+); tetrabutylammonium hydroxide (●). Titrations carried out in the presence of 0.01 M solutions of corresponding (halide) salt.

In order to investigate this, polyacrylic acid was titrated with potassium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide and tetrabutylammonium hydroxide in the absence and presence of neutral salts of the same bases.

A solution of pure polyacrylic acid (molecular weight range 30,000–100,000) was prepared in 0.0128 N concentration. Titrations were performed at 25° in CO_2-free atmosphere using a high pH glass electrode with standard solutions of the bases in the presence and absence of the corresponding (chloride or bromide) salts (0.01 N).

Figure 1a gives the titration curves in the presence of neutral salts; Fig. 1b shows the plots of pH *vs.* log $(1 - \alpha)/\alpha$ for the same cases. The curves in the absence of neutral salt are similar. It is seen that at low values of α the titration curves are similar, but diverge at higher values of α. Table I shows the pH values at half neutralization (pK_a) and the slopes of the best straight lines through the points in the logarithmic plot (n).

An inspection of the titration curves and the pK_a and n values in Table I shows that increasing the size of the cation of the base has the effect of weakening the apparent acid strength of the carboxyl groups; this effect increases with increasing degree of neutralization, as shown by an increasing divergence of the titration curves. The effect is due to the greater loss in electrostatic binding energy when the small hydrogen ion is replaced as a gegenion by a large rather than a small cation, and the fact that a small ion is more effective in shielding the chain than a large ion. Further experimental results involving this and other techniques and a quantitative treatment will be presented later. Parallel experiments on cross-linked polyacrylic acid[4] show similar effects.

TABLE I

	Neutral salt absent		Neutral salt present	
	pK_a	n	pK_a	n
K^+	6.43	2.16	6.00	2.30
Me_4N^+	6.48	2.27	6.18	2.53
Et_4N^+	6.64	2.56	6.29	2.64
Bu_4N^+	6.85	2.69	6.54	2.75

This investigation was supported in part by a research grant, RG 2934(C2) from the Division of Research Grants of the National Institutes of Health, Public Health Service.

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[3] A. Katchalsky, *J. Polymer Sci.*, **7**, 393 (1951).

[4] F. Bernstein, Dissertation, Polytechnic Institute of Brooklyn, 1952.

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, NEW YORK

The Infrared Spectra of Tripropylsilane, Triphenylsilane and Triphenyldeuterosilane

BY LOUIS KAPLAN

RECEIVED JUNE 10, 1954

Although the vibrational spectra of the trihalogenosilanes have been analyzed[1] in detail, there have been relatively few reports in the literature

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[1] See F. Halverson, *Rev. Mod. Phys.*, **19**, 87 (1947).

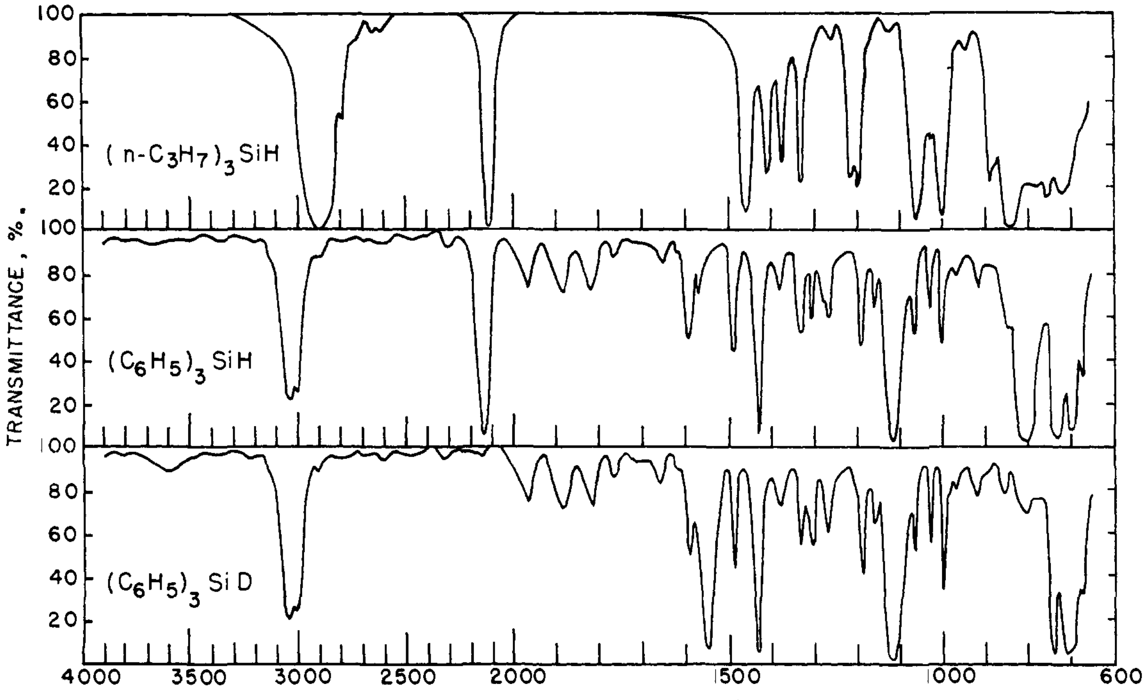

Fig. 1.—Infrared spectra of triorganosilanes.

of the spectra of organosilicon compounds containing silicon–hydrogen bonds. Since a knowledge of vibration frequencies of such bonds in triorganosilanes was of importance in connection with another problem,[2] the infrared spectra of tripropylsilane, triphenylsilane and triphenyldeuterosilane have been measured.

Experimental

The preparation of the silanes is described elsewhere.[2] Infrared spectra were measured on the pure liquids in 0.025 mm. sodium chloride cells using a Perkin–Elmer Model 21 recording spectrophotometer equipped with a sodium chloride prism. The spectra are shown in Fig. 1.

Discussion

The spectra of triphenylsilane and triphenyldeuterosilane are essentially identical except that the strong band at 2135 cm.$^{-1}$ in the former is replaced by one at 1547 cm.$^{-1}$ in the latter, and the band at 805 cm.$^{-1}$ in the former is very much weaker in the latter. The assignment of these bands is unambiguous. The 2135 and 805 cm.$^{-1}$ bands belong to Si–H stretching and bending vibrations, respectively; the 1547 cm.$^{-1}$ band corresponds to Si–D stretching. (The Si–D bending vibration is at too low a frequency for measurement with the instrument used.) The Si–H stretching vibration in tripropylsilane is at 2108 cm.$^{-1}$; the bending vibration is probably at 820 cm.$^{-1}$. For comparison, the Si–H frequencies in trichlorosilane are given[1] as 2258 and 799 cm.$^{-1}$, the corresponding Si–D frequencies being 1647 and 605 cm.$^{-1}$. The lower Si–H stretching frequencies in the triorganosilanes compared to the trihalogenosilanes is not unexpected, since a similar effect has been observed[3] on the C–H vibrations in the substituted methanes.

The bands at 3041 and 3005 cm.$^{-1}$ in the triphenylsilanes and that at 2900 cm.$^{-1}$ in tripropylsilane are clearly due to C–H stretching vibrations. The assignment of the remaining bands is much less certain. It is of interest, however, to compare the spectrum of triphenylsilane with those of other compounds containing phenyl groups attached to silicon.

Richards and Thompson have reported[4] the spectra of some phenyl-substituted silanols and cyclic phenylpolysiloxanes and Young, *et al.*,[5] have also studied a number of the latter. The spectrum of triphenylsilane is strikingly similar to that of triphenylsilanol.[4] Between 1000 and 1350 cm.$^{-1}$ each band in either compound has a corresponding band in the other, the frequencies of which do not differ by more than 5 cm.$^{-1}$. A comparison at higher frequencies is precluded by the absence of a detailed spectrum of the silanol. Between 1350 and 2000 cm.$^{-1}$ the spectrum of triphenylsilane is almost indistinguishable from those[5] of the diphenylcyclosiloxane trimer and tetramer, and points of similarity occur in other regions of the spectra. In particular, the bands at 1590, 1488, 1430, 1190, 1115, 1030 and 1000 cm.$^{-1}$ in triphenylsilane agree closely with those listed[5] by Young, *et al.*, as characteristic of phenyl linked to silicon. The occurrence of the strong band at 1115 cm.$^{-1}$ in triphenylsilane casts doubt on the suggestion[4] of Richards and Thompson that the bands near 1100 cm.$^{-1}$ in the phenylsubstituted silanols and siloxanes are the Si–O stretching vibrations. It is very probable that the intense band near 810 cm.$^{-1}$ observed[4] by

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[2] L. Kaplan and K. E. Wilzbach, THIS JOURNAL, in press.

[3] W. G. Brown, C. J. Mighton and M. Senkus, *J. Org. Chem.*, **3**, 62 (1938).

[4] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949).

[5] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, THIS JOURNAL, **70**, 3758 (1948).

Richards and Thompson in the spectra of organochlorosilanes should be assigned to the Si–H bending vibration rather than, as suggested by them, to a vibration of the Si–Cl bond.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

Improved Procedure for Synthesis of P-32 Phosphorus Oxytrichloride[1]

BY JOSEPH L. KALINSKY AND ALLAN WEINSTEIN

RECEIVED JUNE 1, 1954

The research and development program at this Laboratory on phosphate-type plasticizers and turbine-oil rust inhibitors has made mandatory the obtaining of P-32 labeled phosphorus oxytrichloride of high specific activity and chemical purity. Published methods[2–4] for the synthesis of this intermediate compound suffer from a number of disadvantages, the most important being the need for cumbersome and elaborate equipment, and the loss of from one- to two-thirds of the radioactivity during the synthesis, due considerably to the prolonged contact of $H_3P^{32}O_4$ or metal phosphates with glass at elevated reaction temperatures.

After preliminary unsuccessful attempts to increase the radioactive yield of available procedures by treating PCl_5 with H_3PO_4, HPO_3 and P_2O_5 carrier,[5] respectively, an improved method has been evolved to overcome the above-mentioned difficulties. Use of this procedure has resulted in the synthesis of P-32 phosphorus oxytrichloride with a specific activity of 25 mc./mmole. The material is obtained in 95–99% yield and retains 95–97% of the initial radioactivity. Inactive $POCl_3$ produced by this method was assayed at 97 ± 1% purity, by determination of chloride and phosphate.

Quantities as small as 0.40 g. (0.27 ml.) of the compound have been successfully prepared. The total time required for all operations is from 4 to 8 hours, depending upon the specific activity level desired.

Experimental

A typical run is described below.

Dehydration of Aqueous P-32 Phosphoric Acid.—Ten millicuries of an aqueous solution of P-32 phosphoric acid[6] with a specific activity of 0.025 mg. P/mc. (5.8 mc./ml. of solution), O.R.N.L. Cat. No. P-32 P-1, was transferred to a tared 25-ml. two-necked flask possessing ₸ 19/22 joints. One neck was stoppered, and the other fitted with a still head, a 105° angle vacuum adapter and an appropriate receiver, and lyophilization of the solution to a residue of 0.224 g. (12.4 mmoles) was accomplished by application of a vacuum and suitable freezing baths. Lyophilization of the solution beyond about 0.05 g. is possible, but impractical; for samples of this size, calculation of the millimoles of reactants would include millimoles of $H_3P^{32}O_4$, neglected above.

Synthesis of P-32 Phosphorus Oxytrichloride.—The stopper and adapter were replaced by a double-surface condenser with attached drying tube and a hopper, which was constructed from a ₸ 19/22, double jointed drying tube by grinding a slightly oversized glass rod into the barrel with emery and alundum. The rod was held firmly in place by use of a sleeve adapter on the top joint and a short length of rubber tubing.

The hopper was charged with 2.70 g. (13.0 mmoles) of reagent grade PCl_5, and the P-32 $H_3P^{32}O_4$ was frozen by immersion of the flask in a Dry Ice–acetone-bath. The reaction was initiated by adding a small quantity (*ca.* 0.1 g.) of PCl_5, removing the freezing bath, and allowing the mass to thaw slightly. The cycle of alternate freezing and addition of PCl_5 was continued until the reaction was controllable without freezing; the remainder of the PCl_5 was then added as rapidly as possible.

The flask was then allowed to warm to room temperature and cautiously brought to reflux for a period of 15 minutes. The flask was then cooled, and immersed in the Dry Ice–acetone-bath; warm water was circulated through the condenser, to distil any adhering P-32 $POCl_3$ into the flask. The flask was then fitted for lyophilization, run at 1 mm. pressure, maintaining the temperature of the still flask at −5°; yield 1.89 g. (99% of theoretical) of P-32 $POCl_3$ of specific activity 0.78 mc./mmole (96% activity retained) with a chemical purity of 97 ± 1%. The specific activity of the compound was determined by conversion into P-32 tricresyl phosphate and an assay thereof.

Acknowledgment.—The authors wish to acknowledge with great appreciation the efforts of Mr. A. R. Allison of this Laboratory and Mr. V. Saitta of the Bureau of Ships, Washington, D. C., in fostering the application of radioisotopes to naval material development.

MATERIAL LABORATORY
NEW YORK NAVAL SHIPYARD
BROOKLYN, NEW YORK

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[1] The opinions or assertions herein are those of the authors, and are not to be construed as reflecting those of the Navy Department or the Naval Service at large.

[2] B. Axelrod, *J. Biol. Chem.*, **176**, 295 (1948).

[3] J. E. Gardiner and B. A. Kilby, *Research*, **2**, 590 (1949).

[4] J. E. Gardiner and B. A. Kilby, *J. Chem. Soc.*, 1769 (1950).

[5] J. L. Kalinsky and B. Gilbert, unpublished work, showed that one-third of the radioactivity was retained by the reaction flask.

[6] Obtained from the Carbide and Carbon Chemical Co., Oak Ridge, Tennessee.

The Ammonolysis of Hexachlorodisiloxane

BY WALTER C. SCHUMB AND ROBERT A. LEFEVER

RECEIVED JUNE 28, 1954

A study of the ammonolysis of Si_2OCl_6 and of the pyrolysis of the product was undertaken, following similar studies which have been reported with $SiCl_4$,[1–3] with Si_2Cl_6,[4] and with $SiHCl_3$.[5] It was expected in view of the earlier work that ammonolysis of hexachlorodisiloxane, Si_2OCl_6, should lead to $(Si_2ON_3H_3)_x$ at room temperature, and that this product on heating should form an oxynitride, $(Si_2ON_2)_x$. Compounds of silicon containing oxygen and nitrogen have been reported,[6] but oxygen in these cases was believed to be present as silica contamination.

Experimental

All reactions were carried out in carefully dried apparatus with a minimum of atmospheric exposure. Several samples of hexachlorodisiloxane were obtained, some from commercial sources, another from Dr. Herbert H. Anderson, and some by preparation as required. They were purified by fractional distillation (b.p. 134° at 760 mm.) and kept in sealed glass tubes. When needed, these tubes were cooled in liquid nitrogen, opened and sealed to the apparatus with Cenco Plicene. The apparatus was evacuated and the sample distilled into the reaction vessel under reduced pressure.

Commercial ammonia was distilled into a storage tube, in which it was dried over sodium; before use of the ammonia, non-condensable gases were pumped off.

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[1] F. Lengfeld, *Am. Chem. J.*, **21**, 531 (1899).

[2] E. Vigouroux and Hugot, *Compt. rend.*, **136**, 1670 (1903).

[3] M. Blix and W. Wirbelauer, *Ber.*, **36**, 4220 (1903).

[4] R. Schwarz and W. Sexauer, *ibid.*, **59B**, 333 (1926).

[5] O. Ruff and E. Geisel, *ibid.*, **38**, 2235 (1905).

[6] L. Weiss and T. Engelhardt, *Z. anorg. allgem. Chem.*, **65**, 38 (1909).