($D_{2}^{3}d$). Space group $P\bar{4}2_1$ does not permit a tetrahedral arrangement of atoms around the phosphorus atom. Since the structure appeared to be isotypic with tetramethylammonium dichloroiodide[4] and since the Patterson projection could be explained on the basis of this structure, the structure based on $P\bar{4}2_1m$ was chosen.

Crystal Structure.—Using ($hk0$) data, a Patterson projection was made on ($00l$) and the approximate x- and y-parameters determined. From these parameters the signs of the $F(hk0)_{\text{obsd}}$ were calculated and used in a Fourier projection on ($00l$). The x- and y-parameters were refined as much as possible by a repetition of this Fourier projection. The z-parameters were obtained from a Patterson projection on (110). In order to obtain better agreement between the calculated and observed F values, an empirical temperature correction factor of the form $e^{-1.51 \sin^2\theta}$ was applied to the calculated F values. It was felt by the authors that the usual scheme of computing R_1 does not make sufficient allowance for reflections, which, while not zero, are not sufficiently strong to record on film with ordinary exposures. Accordingly, a slightly modified method of calculating the R_1 values, consisting of assigning each absent or unobserved reflection an F value which was calculated as follows, was used. The minimum intensity observable was corrected by the angle factors corresponding to each of the unobserved reflections. Taking one-half of the square roots of the quantities thus obtained yielded F values which were arbitrarily assigned to the absent reflections for the purpose of calculating R_1. The R_1 calculated in this manner is defined as R_1^*. Using the parameters chosen an R_1^* value of 0.27 was obtained.

The compound proved to be isostructural with tetramethylammonium dichloroiodide,[4] with the following atoms at the following positions of space group $D_{2}^{3}d$-$P\bar{4}\,2_1m$: 2 P at (b) ($0\ 0\ {}^1/_2$), (${}^1/_2\ {}^1/_2\ {}^1/_2$); 2 I at ($c$) ($0\ {}^1/_2\ z$), (${}^1/_2\ 0\ \bar{z}$) with $z = 0.161$; 4 Cl at (e) $x, {}^1/_2 + x, z;\ \bar{x}, {}^1/_2 - x, z;\ {}^1/_2 + x, \bar{x}, \bar{z};\ {}^1/_2 - x, x, \bar{z}$ with $x = 0.18_0$, $z = 0.16_1$; 8 Cl at (f) $xyz;\ {}^1/_2 - x, {}^1/_2 + y, \bar{z};\ \bar{x}\bar{y}z;\ {}^1/_2 + x, {}^1/_2 - y, \bar{z};\ \bar{y}x\bar{z};\ {}^1/_2 + y, {}^1/_2 + x, z;\ y\bar{x}\bar{z};\ {}^1/_2 - y, {}^1/_2 - x, z$ with $x = 0.15_5$, $y = 0.07_9$, $z = 0.29_8$.

This structure consists of regularly tetrahedral PCl_4^+ ions, and linear $ClICl^-$ ions with the interatomic distances in ångström units are

P–8-fold Cl	1.98
I–4-fold Cl	2.36
8-fold Cl–8-fold Cl (within PCl_4^+ tetrahedra)	3.23
8-fold Cl–8-fold Cl (from one PCl_4^+ to the next)	3.50
4-fold Cl–8-fold Cl	3.56

Extensive calculations of intensities based on selected chlorine positions near those given above showed that the positions of chlorine atoms could be changed considerably without affecting the R_1^* value. For example

x for 4 (e)	0.16	0.17	0.18	0.19	0.20
R_1^*	.285	.271	.270	.272	.277

DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

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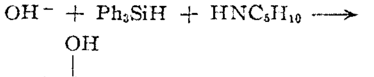
COMMUNICATIONS TO THE EDITOR

HYDROGEN ISOTOPE EFFECT IN THE HYDROLYSIS OF TRIPHENYLSILANE

Sir:

Recently, Gilman, Dunn and Hammond reported[1] that triphenylsilane-*d* was hydrolyzed in moist piperidine "almost six times faster than its protium analog." They attributed this unusual isotope effect to the displacement of a hydride ion in such a manner that a hydrogen–hydrogen bond of considerable strength is present in the transition state of the reaction. This picture of the reaction path might be formulated as



$$OH^- + Ph_3SiH + HNC_5H_{10} \longrightarrow \overset{\displaystyle OH}{\overset{|}{Ph_3Si}}\text{---}H\text{---}H\text{---}NC_5H_{10} \longrightarrow Ph_3SiOH + H_2 + C_5H_{10}N^-$$

Because of the unusual effect reported for this reaction, we have examined several similar reactions which involve the formation of hydrogen, presumably by abstraction of a hydride ion. To enhance any isotope effects, tritium, rather than deuterium, was used in competitive measurements of k_T/k_H, the ratio of the isotopic reaction rates.

The alkaline alcoholic hydrolysis[2] of tripropylsilane-*t* was found to be about 0.7 as fast as that of its protium analog. The alcoholysis of lithium aluminum hydride-*t*[3] and of lithium borohydride-*t*[4] did not give consistent values of k_T/k_H, possibly because of changes in the reacting species; the observed values fell between 1.2 and 0.8.

In view of these results we have reinvestigated the hydrolysis of triphenylsilane in moist piperidine. Tritium-labeled triphenylsilane was prepared[5] by the reduction of triphenylchlorosilane with lithium aluminum hydride-*t*.[3] The triphenyl-silane-*t* was dissolved in a 1.0 *M* solution of water in piperidine, in a previously evacuated system, and permitted to react at 25°. At intervals, the reaction was stopped by cooling to −80°, and the evolved hydrogen was collected. The volume of each fraction was measured manometrically and its tritium content was determined in an ion chamber with a vibrating reed electrometer. The total volume and tritium content of the fractions agreed with those expected from analysis[5] of the triphenylsilane-*t* by hydrolysis with moist piperidine and potassium hydroxide. The experimental results are given in Table I. The ratio of the rate constants is calculated for each gas fraction from the expression

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$$\frac{k_T}{k_H} = \frac{d(\mathrm{HT})}{d(\mathrm{H_2})} \times \frac{(\mathrm{Ph_3SiH})}{(\mathrm{Ph_3SiT})} = \log \frac{(\mathrm{HT})_\infty - (\mathrm{HT})_2}{(\mathrm{HT})_\infty - (\mathrm{HT})_1} \Big/ \log \frac{(\mathrm{H_2})_\infty - (\mathrm{H_2})_2}{(\mathrm{H_2})_\infty - (\mathrm{H_2})_1}$$

where $(\mathrm{HT})_t$ refers to the amount of tritium and $(\mathrm{H_2})_t$ to the volume of gas collected up to time t. The average value of k_T/k_H, over the course of more than 40% reaction is 0.796 ± 0.004.

This result is in good agreement with a theoretical value of 0.8 calculated[6,7] considering only the stretching frequencies of the Si–H and H–H bonds in the proposed model. The corresponding theoretical value of k_D/k_H is 0.9.

TABLE I

HYDROLYSIS OF TRIPHENYLSILANE-*t*

Fraction	Reaction cumulative %	H_2, mmole	HT, μcuries	HT/H_2, μcuries/ mmole	k_Tk_H
1	16.2	0.286	20.9	73.1	0.803
2	24.8	0.151	11.2	74.2	0.792
3	40.6	0.279	21.5	77.1	0.794
4	100.0	1.046	104.0	99.4	
Total		1.762	157.6	89.4	

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ARGONNE NATIONAL LABORATORY
P. O. BOX 299
LEMONT, ILL.

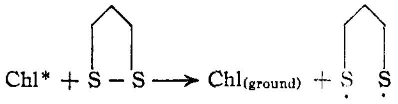
LOUIS KAPLAN
KENNETH E. WILZBACH

RECEIVED OCTOBER 1, 1952

A POSSIBLE PRIMARY QUANTUM CONVERSION ACT OF PHOTOSYNTHESIS[1,2]

Sir:

To account for the observation[3,4,5] that illumination prevents the appearance of newly assimilated carbon in the compounds of the tricarboxylic acid cycle, it was suggested[5] that the light shifts the steady-state condition of the thioctic acid-containing coenzyme[6,7] (protogen, lipoic acid, thioctic acid, P.O.F.) toward the reduced (dithiol) form, in which condition it is incapable of oxidatively decarboxylating pyruvic acid,[8,9] newly formed from CO_2, to give rise to the acetyl-CoA[10,11,12] required to bring this carbon into the compounds of the Krebs cycle. We are here reporting some observations leading to the further suggestion that this shift toward the dithiol form is the *direct* result of the light action and that a biradical formed by dissociation of the disulfide bond in a strained five-membered disulfide containing ring (as in 6,8-thioctic acid and trimethylenedisulfide) is the species in which the quantum absorbed by the plant pigments and stored as electronic excitation in chlorophyll[13] appears first as chemical bond potential energy; *i.e.*, that a possible primary quantum conversion act of photosynthesis is represented by the equation



(I)

Subsequent abstraction of H atoms[14,15] from a suitable donor by the thiyl free radicals would lead to the dithiol which would be reoxidized ultimately by CO_2. The residual oxidation product of the H donor would lead in the end to molecular oxygen. It is obvious that on both the reductant and oxidant sides the chemical products of the conversion of several quanta will be required to accomplish the reduction of each CO_2 molecule and the generation of each O_2 molecule.

These subsequent reactions, being strictly chemical, may lead to diverse energy rearrangements. For example, the chemical potential of reduced carbon might be converted by oxidative phosphorylation reactions into the energy of phosphoric anhydrides which, in turn, could raise the potential energy of intermediates in the reaction sequences leading to the evolution of molecular oxygen and to the reduction of CO_2.[16,17]

A value of the dissociation energy for this particular disulfide link lying in the region of 30–40 kcal. would constitute not only permissive evidence for reaction (I) but positive evidence in its support, since hitherto it has been difficult to suggest any likely primary chemical step capable of usefully absorbing the greater part of the ≃ 30–40 kcal. quantum of electronic excitation available for photosynthesis. Estimates of D(RS-SR) from simple open chain compounds range from 50[18] to 70[19] kcal. However, the fact that 5,8-thioctic acid is colorless, while 6,8-thioctic acid is yellow,[20] suggested that the incorporation of the S—S bond into a 5-membered ring might indeed introduce sufficient strain into it so as to reduce the S—S dissociation energy by as much as 25–30 kcal., thus bringing it down into the required range. A number of experiments have been performed using the product of the reaction of Na_2S_2 with $(CH_2)_3Br_2$ (trimethylenedisulfide) as a model substance. Its

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(1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

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