all considerably lower than the corresponding values calculated from Fig. 4. Evidently, therefore, the change in the I/I_0 ratio with pressure can only partially account for the deviations from linearity of the curves in Fig. 4. No explanation suggests itself for the marked increase in curvature as the wave length decreases.

The shape of Fig. 5 suggests that the absorption curve is a combination of two distinct curves, indicating different processes of absorption at long and short wave lengths. This is further confirmation of the conclusion reached above, that the decomposition proceeds by two different mechanisms, one predominating at long wave lengths and the other at short wave lengths.

Summary

Oxalyl chloride decomposes slowly when illuminated with light of any wave length below 3800 Å. The reaction is predominantly unimolecular, and has a low quantum yield. The final products of decomposition are phosgene and carbon monoxide, but various lines of evidence indicate that the initial products are chlorine and carbon monoxide.

Most of the experimental observations can be explained satisfactorily by assuming that oxalyl chloride decomposes by two different mechanisms. When illuminated with light of short wave length, the molecule breaks at the carbon–carbon bond; with light of longer wave length a break at one of the carbon–chlorine bonds predominates.

The absorption coefficients of oxalyl chloride have been measured between 3700 and 2400 Å.

BERKELEY, CALIFORNIA RECEIVED JANUARY 3, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF STANFORD UNIVERSITY]

The Photolysis of Lead Tetramethyl and Lead Tetraphenyl[1]

BY PHILIP A. LEIGHTON AND RAYMOND A. MORTENSEN

The discovery by Midgley and Boyd[2] in 1922 that a trace of lead tetraethyl will prevent detonation in internal combustion engines and its use for that purpose has provided incentive for a rather extensive study of the pyrolysis of this and related compounds. Observations on the photochemical reactions of these substances, however, seem to have been limited to the fact that long exposure to sunlight or ultraviolet light results in a decomposition, with a separation of metallic lead.[3,4] The present paper reports a study of the photochemical decomposition of lead tetramethyl and tetraphenyl, together with a few observations on lead tetraethyl.

Absorption Spectra

In agreement with the observations of Terenin[4] and of Duncan and Murray[5] all three compounds were found to show only continuous absorption. For example, in Fig. 1 is reproduced a microphotometer tracing of an absorption photograph of lead tetramethyl vapor. A 40-cm. absorption tube was used and the pressure of the vapor varied by changing the temperature of a side tube containing liquid (or solid) lead tetramethyl. The approximate long wave length absorption limits observed, both in the vapor and in trimethylpentane solutions, were

Pb(CH$_3$)$_4$ vapor	2800 Å.
Pb(CH$_3$)$_4$ solution	3100
Pb(C$_2$H$_5$)$_4$ vapor	3500
Pb(C$_2$H$_5$)$_4$ solution	3500
Pb(C$_6$H$_5$)$_4$ solution	2800

Products of Decomposition

Lead tetramethyl and tetraethyl, in octane solutions, in the pure liquid, and in the vapor, were decomposed by the absorption of radiation in the ultraviolet absorption band. In solutions, or in the pure liquids, when air and moisture were not excluded, upon exposure a distinct turbidity appeared, followed by the separation of a grayish-white solid, and finally by the formation of a black deposit on the walls of the vessel. When the material was carefully dried and sealed from the atmosphere, the black deposit formed from the start. Lead tetraphenyl, in benzene and hexane solutions, showed the same phenomena. The black deposit had the properties of metallic lead;

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago meeting, September, 1933.

[2] Midgley and Boyd, *J. Ind. Eng. Chem.*, **14**, 894 (1922).

[3] Calingaert, *Chem. Rev.*, **2**, 43 (1925).

[4] Terenin, *J. Chem. Phys.*, **2**, 441 (1934).

[5] Duncan and Murray, *ibid.*, **2**, 640 (1934).

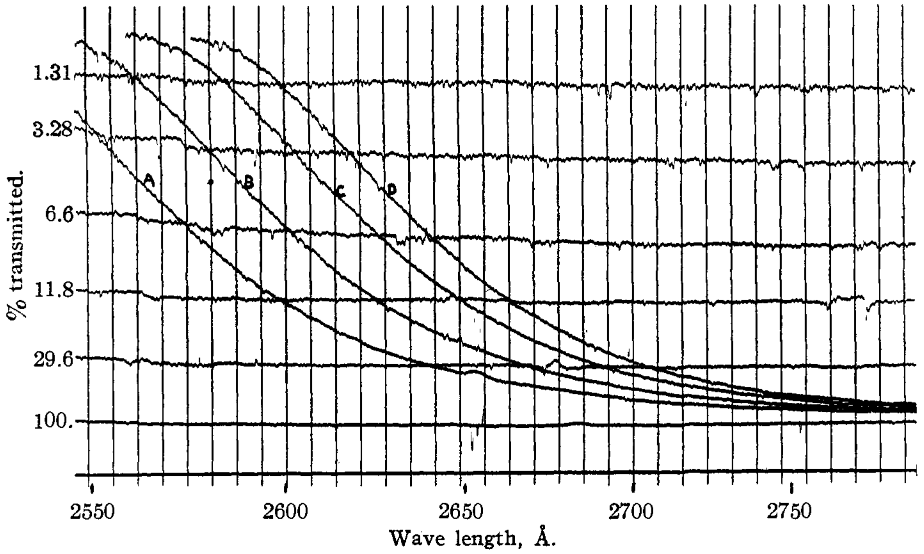

Fig. 1.—Absorption of lead tetramethyl vapor. Tracings A, B, C, D, represent the absorption of lead tetramethyl at 5.4, 8.3, 15.3 and 25.4 mm. pressure (d. = 40.0 cm.). Ordinates are tracings of the spectra of the source alone, and source plus neutral screens the transmissions of which are given.

the whitish precipitate obtained in presence of air and moisture was not identified; it was presumably lead oxide or hydroxide.[6,7]

The gaseous products from the lead tetramethyl decomposition were found by analysis to consist chiefly of ethane. A considerable amount of pure diphenyl was separated, by evaporation and extraction with alcohol, from a solution of lead tetraphenyl in hexane which had been exposed for several hours to ultraviolet radiation. Lead tetraphenyl thermally decomposed at 400° in a closed tube gave only metallic lead and diphenyl. It may be concluded that in the case of lead tetramethyl and lead tetraphenyl the principal overall reaction in photodecomposition is

$$PbR_4 \longrightarrow Pb + 2R_2$$

The hydrocarbon products from the photodecomposition of lead tetraethyl were not examined.

The immediate formation of particles of metallic lead upon irradiation of the solutions of all three compounds was demonstrated by means of a slit ultramicroscope equipped with a quartz cell, after Siedentopf and Zsigmondy.[8]

A concentrated beam of visible light was passed into the cell from one side, and a beam of ultraviolet radiation from which visible light had been largely removed by focal isolation from another. After a few seconds of exposure hundreds of thousands of ultramicroscopic particles appeared, which rapidly coagulated to larger particles and precipitated or plated out of the solution. Upon irradiation of lead tetramethyl vapor, although lead plated out on the walls of the vessel, no particles of as large as ultramicroscopic dimensions could be observed in the gas phase.

Application of the Method of Radioactive Indicators

The separation of metallic lead during the reaction, with its resultant light absorption and scattering, means that the amount of decomposition, in absolute quantity, must be kept small in the determination of quantum yield. Ordinary analytical methods proving inadequate for the estimation of the small quantities involved, the method of radioactive indicators was employed.

Of the four radioactive isotopes of lead, radium D was chosen as being more readily available and as having the most suitable half-life period, although it has the disadvantage that some time must elapse before reliable electroscope readings can be made. The radium D was obtained from spent emanation tubes, several hundred of which were pulverized and heated to about 400° to drive off any mercury retained in the tubes. The material was then treated with a few cc. of hot hydrochloric acid containing a small amount of lead chloride, the solution decanted, and evaporated to dryness. Several grams of lead chloride was

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(6) Nordenson and Haber, *Kolloid Beihefte*, **7**, 91 (1915).

(7) Haber, *Trans. Am. Electrochem. Soc.*, **2**, 190 (1902).

(8) Siedentopf and Zsigmondy, *Ann. Physik*, **10**, 1 (1903).

added to the residue and the whole boiled with enough distilled water to ensure complete solution. Upon cooling in ice, crystals of lead chloride, containing a small amount of radium D chloride, separated out.

The radioactive lead chloride so obtained was used to prepare lead tetramethyl and lead tetraphenyl. Lead tetramethyl was prepared after the method of Grüttner and Krause,[9] using methylmagnesium bromide. As the yield was never more than a few tenths of a cc., a small fractionation flask, similar to the one described by Emich[10] was employed. The product boiled at 108–109°, and showed n^{18}D 1.5130. Lead tetraphenyl was prepared by the method of Pfeiffer and Truskier,[11] using phenylmagnesium bromide. The crystals of lead tetraphenyl were purified by two recrystallizations from benzene, followed by sublimation, the sublimate being washed with benzene to remove traces of diphenyl. The product had a very sharp melting point at 224°. Several attempts to prepare small quantities of radioactive lead tetraethyl met with indifferent success, the product invariably giving evidence of impurity. The metallic lead which separated during the preparations was recovered by treating with hot nitric acid, cooling in ice, and precipitating with hydrochloric acid.

Since the β-radiation from radium D is too feeble to appreciably affect an ordinary electroscope, it is necessary to rely on the radiation from its disintegration products, radium E and F, for observation. Using the treatment of Rutherford[12] it can be shown that, starting with pure radium D, the radium E concentration, and hence the β-activity, will reach a maximum in fifty-three days, while approximate equilibrium, with activity within 1% of the maximum, is established in about thirty days. The corresponding times for radium F (α activity) are eight hundred and forty days and about seven hundred days. In this work, amounts of radium D were compared by means of a β-ray electroscope after allowing the samples to stand for thirty days.

A low capacity gold leaf electroscope, especially suited to the required measurements, was constructed. Uniformity of behavior was increased by attaching the leaf with a brass clip rather than adhesive. The electroscope was charged from a 250 v. d. c. source, and the natural leak was kept below 0.3 v. per minute. The same divisions of the scale were always used, and the assumption that the rate of fall is proportional to the activity of the source was verified. The rate due to leakage was subtracted from the total. Measurements were compared against known standards, which contained usually about 1 mg. of the lead–radium D mixture. Samples of as small as 0.03 mg. of lead could be estimated with a probable error of less than 2% by taking the mean of several readings.

Quantum Yields

Quantum yields for the reaction were determined in one wave length region only—the band centering at 2537 Å. from a high pressure mercury arc (resonance radiation almost completely reversed) separated from other lines by means of a Cornu prism monochromator of conventional design. Radiation emerging from the exit slit of the monochromator, rendered slightly convergent by a third lens, passed through a rectangular fused silica reaction cell of dimensions 11 × 26 × 36 mm. and onto a large Moll surface thermopile. Precautions described earlier[13] were observed in the use of the thermopile. The proper size and shape of the stop to be used over the pile were determined by inserting a piece of blue print paper at that point and exposing it for about one-half hour. During experiments in solutions the radiation was passed through the 11-mm. dimension of the cell and it was continually shaken in a sidewise direction with a mechanical shaker. During experiments in the vapor the radiation was passed through the 26-mm. dimension of the cell. Measurements were made on lead tetraphenyl in *n*-hexane solutions and on lead tetramethyl in octane (2,2,4-trimethylpentane) solutions and in the vapor.

Lead Tetraphenyl.—The solubility of lead tetraphenyl in paraffin hydrocarbons is slight, and this solubility, as determined by the method of radioactive indicators for several hydrocarbons (Table I), led to the choice of *n*-hexane as the solvent.

Solutions, with air and moisture excluded, were prepared in the apparatus shown in Fig. 2. A weighed amount of lead tetraphenyl was placed in the silica cell C, which was then sealed to the system with silica–glass seals. *n*-Hexane was placed

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[9] Grüttner and Krause, *Ber.*, **49**, 1125 (1916); Krause, *ibid.*, **62**, 1877 (1929).

[10] Emich, *Monatsh.*, **53**, 54, 312 (1929).

[11] Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904).

[12] Rutherford, "Radioactive Substances and their Emanations," Cambridge University Press, Cambridge, England, 1913.

[13] P. A. and W. G. Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

TABLE I

SOLUBILITY OF LEAD TETRAPHENYL AT 25°

Solvent	Solubility G. per 100 cc.	Mole per liter
n-Hexane	0.0143	0.000278
"Hexane" from petroleum	.0134	.000260
2,2,4-Trimethylpentane	.0121	.000234

in flask F and thin pieces of freshly cut sodium added. The flask was sealed at H and allowed to stand until evolution of gas had ceased, then cooled to 0° while the system was alternately evacuated through P and flushed with pure dry nitrogen through N. Flask F was then warmed and the reaction cell C cooled until it was filled with hexane, when it was sealed off at E. The solution in C was frozen and pumped several times, then the cell sealed at D, removed, warmed in order to bring all of the lead tetraphenyl into solution, cooled to room temperature, and placed in the monochromator. Solutions with air and moisture not excluded were made by adding lead tetraphenyl and undried hexane directly to the reaction cell, without evacuation and without sealing.

The usual energy measurements before, during, and after exposure were made, and quantum yields were calculated by means of standard equations, allowing for absorption by reaction products.[14] During irradiation the transmission decreased rather rapidly at first as a suspension of solid particles was formed, then increased slightly as this suspension flocculated and settled out. Since these changes were due partly to absorption and partly to scattering, and were rather irregular in nature, some irregularity was introduced into the quantum yields, particularly when air and moisture were excluded.

After the desired exposure, the cell was opened and the solution washed with warm hexane into a Whatman No. 50 filter. This grade of filter was found to retain the solid suspension completely. After thorough washing with hexane, the filter and residue were transferred to a porcelain dish. The cell was washed with hot nitric acid and this was added to the residue. After standing for thirty days, the filter paper was slowly ignited, and the beta activity of the residue was compared with that of a known standard. Ignition was delayed because the beta emitting element, radium E, is an isotope of bismuth and hence less volatile than lead. Blanks with no exposure gave no beta activity; with sufficient exposure to produce complete decomposition the activity corresponded to that expected from the total amount of lead tetraphenyl originally present. The results are given in Tables II and III.

TABLE II

LEAD TETRAPHENYL DECOMPOSITION IN HEXANE, OXYGEN AND MOISTURE NOT EXCLUDED

Concn. of solution, mols/liter	% decomposed	Quanta absorbed $\times 10^{-17}$	Molecules decomposed $\times 10^{-17}$	Quantum yield
0.000146	9.7	3.68	0.82	0.22
.000146	13.3	4.86	1.12	.23
.000146	28.9	9.59	2.44	.25
.000146	44.8	17.8	3.78	.21
			Mean	.23

TABLE III

LEAD TETRAPHENYL DECOMPOSITION IN HEXANE, OXYGEN AND MOISTURE EXCLUDED

Concn. of solution, mols/liter	% decomposed	Quanta absorbed $\times 10^{-17}$	Molecules decomposed $\times 10^{-17}$	Quantum yield
0.000055	38	3.89	1.19	0.31
.000090	51	5.91	2.62	.44
.000081	60	7.99	3.32	.40
.000109	64	12.6	4.05	.32
			Mean	.37

If any trend with either percentage decomposed or concentration exists, it is overshadowed by the variations resulting from irregularity in transmission.

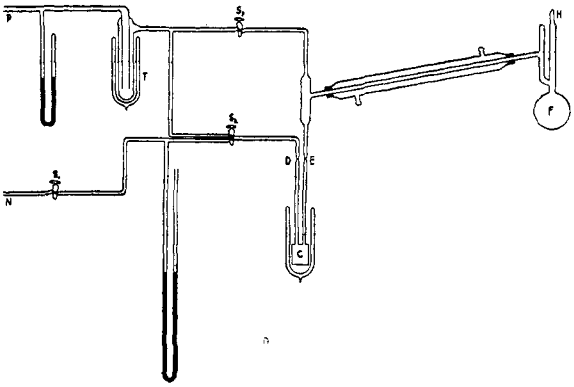

Fig. 2.—Apparatus for preparing solutions of lead tetraphenyl in hexane.

Lead Tetramethyl in Trimethylpentane.—2,2,4-Trimethylpentane was chosen as a solvent for lead tetramethyl because its boiling point (99°), being near that of the solute, made it well suited to the method of analysis adopted. The solvent was dried over sodium, decanted and distilled, and the solutions were prepared directly in the silica reaction cell.

Irradiation was carried out as for lead tetraphenyl, after which the contents of the cell were

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(14) Leighton and Forbes, THIS JOURNAL, 51, 3549 (1929).

transferred to a shallow dish and the solvent, together with unchanged solute, evaporated under reduced pressure. Any lead retained by the walls of the cell was removed with hot nitric acid and added to the residue and the acid slowly evaporated to dryness. After thirty days the β-activity was determined and the amount of lead calculated.

The transmission, unlike the case of lead tetraphenyl, increased at first, then decreased. This difference may be due partly to the fact that diphenyl absorbs strongly at 2537 Å. while the hydrocarbon products from lead tetramethyl do not, and partly to a difference in the character of the suspension when both solute and solvent are changed. Owing to this irregularity, quantum yields calculated by means of the equations used for lead tetraphenyl showed such variation that the method of extrapolation to zero exposure was employed. This method has the advantage that no allowance for absorption by the products need be made in calculating the individual Φ's.

The results are given in Fig. 3. The limiting values of Φ at zero exposure are 0.37 and 0.42 for the 0.00067 *M* and 0.00278 *M* solutions, respectively.

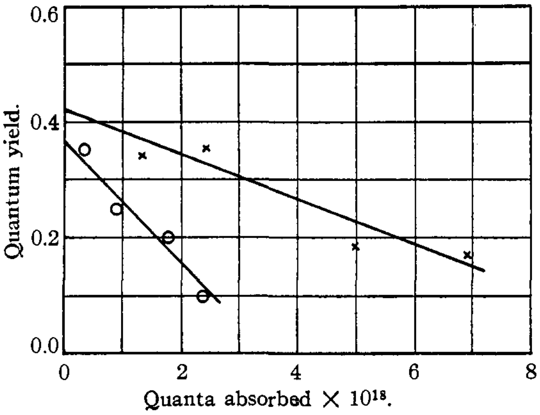

Fig. 3.—Extrapolation of quantum yields in the photolysis of lead tetramethyl in trimethylpentane: circles, 0.00067 *M* solutions; crosses, 0.00278 *M* solutions.

Lead Tetramethyl Vapor.—The apparatus shown in Fig. 4 was used. A small amount of liquid lead tetramethyl was poured into the bulb B through a long stem funnel inserted at A. The liquid was then frozen in B and the system sealed at A. Reduction of the vapor pressure by freezing is a necessary precaution on account of the explosive character of the vapor. While the liquid was frozen, the system was evacuated *via* P. After evacuation the lead tetramethyl was allowed to warm to such temperature (controlled *via* thermostat) that its vapor pressure, measured on M, had reached the desired value. The reaction cell, C, was then filled with the vapor at that pressure by turning stopcock S_1 and the irradiation commenced. After exposure, the surplus vapor was removed by breaking the capillary tip at E and passing a gentle stream of purified nitrogen (introduced *via* N) through the cell. Resealing and pumping the cell for complete removal of the vapor proved unnecessary. The cell was next detached from the system at H and the lead film on the walls dissolved in hot nitric acid. The solution was transferred to a shallow dish, evaporated, and the amount of lead determined as before.

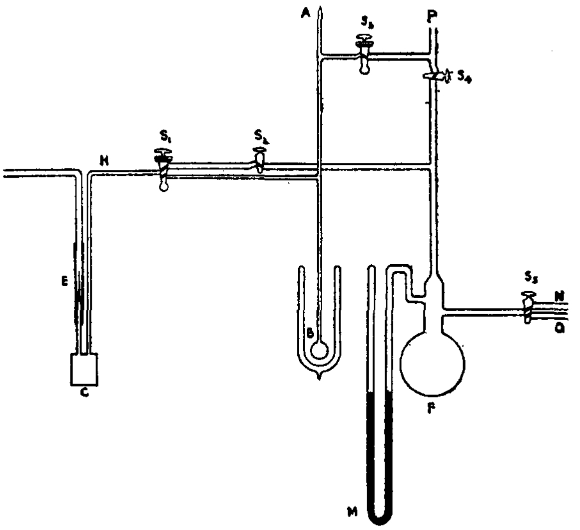

Fig. 4.—Apparatus for use with lead tetramethyl vapor.

Several experiments were performed in which oxygen under known pressure was also admitted to the reaction cell. To accomplish this, tank oxygen, purified and dried, was introduced at O and passed into the storage flask F to the desired pressure. By opening S_1 to F, the cell, previously filled with lead tetramethyl vapor, received oxygen until the total pressure was equal to that of oxygen alone in F.

During irradiation, absorption of light by the film of lead plated on the walls soon became noticeable. Accurate allowance for this could not be made in calculation because it was unevenly distributed between the front and back windows of the cell. Mounting platinum electrodes inside the cell with a 100-v. d. c. potential between them caused practically all of the lead to deposit on the electrodes rather than the walls, but this procedure was abandoned on account of the possibility of spurious effects being introduced by the presence of platinum electrodes and electric potential. Instead, advantage was taken of the highly sensitive analytical method by reducing the time of exposure until the error due to light absorption by the lead film became negligible. Thus, after an eleven-minute exposure, the 0.03 mg. of lead deposited reduced the transmission of the cell only 8%. This small absorption by the lead films made it possible to assume with small error in calculating the quanta absorbed by the vapor that the deposit was equally distributed. Neglecting the film entirely changed the values of Φ by less than 2%.

The results obtained are presented in Table IV. Temperatures varied from 25 to 29° during the exposures.

TABLE IV

PHOTOLYSIS OF LEAD TETRAMETHYL VAPOR

Pressure of vapor, mm.	Pressure of oxygen, mm.	Exposure, sec.	Quanta absorbed $\times 10^{-16}$	Molecules decomposed $\times 10^{-16}$	Quantum yield	
22	0	957	7.43	8.10	1.09	1.11
22	0	1258	9.52	10.7	1.13	
31	0	650	6.54	7.58	1.12	1.11
31	0	976	10.0	11.0	1.10	
29	9.5	635	8.46	9.1	1.07	
29	17.6	646	7.25	7.5	1.03	
29	33.2	644	7.84	8.0	1.02	
29	81.0	638	7.97	8.1	1.01	

Remarks on Quantum Yields.—The quantum yield, 1.11, found for lead tetramethyl vapor in absence of oxygen differs from unity by an amount slightly greater than the probable error, indicating that short chains or an occasional second molecule are involved in the reaction. Within narrow limits, 22 to 31 mm., the quantum yield appears to be independent of pressure. Oxygen reduces the quantum yield, the value of unity being approached as oxygen pressure is increased. Smaller quantum yields in solution in inert solvents show that deactivation or recombination becomes important under those conditions. The ability of free methyl groups (*vide infra*) to react with metallic lead should lead to some recombination with reduction of quantum yield in the vapor also, so that the observed value of 1.11 may represent the balance between a considerable recombination and a considerable chain length. Oxygen, by removing methyl groups, would retard both the recombination and the chain, bringing the quantum yield toward unity, as observed. It is interesting that lead tetramethyl in trimethylpentane and lead tetraphenyl in hexane give almost identical quantum yields.

The Production of Free Radicals during Photolysis

The well known experiments of Paneth[15] and his co-workers have demonstrated that free methyl radicals are produced during the thermal decomposition of lead tetramethyl vapor. The continuous absorption of this compound indicates a dissociation as the primary process of the photodecomposition, and it becomes of interest to determine whether free hydrocarbon radicals are produced during this process also.

If a concentrated beam of ultraviolet radiation be substituted for the heating furnace in Paneth's apparatus, a different order of concentration of free radicals is to be expected. Not only is the number of quanta entering the tube small compared to the number of molecules passing along it, but at the low pressures necessary to observe free radicals light absorption is weak and the light path is necessarily short. A simple calculation shows that with a mercury arc delivering 10^{16} quanta/sec. of λ 2537 Å. to the reaction tube the amount of lead removed from a lead mirror some 10 cm. from the point of illumination would scarcely be more than 0.01 mg. per hour, which is much smaller than the amount of metal usually removed in experiments of the Paneth type.

This difficulty may be overcome by using, instead of ordinary lead, a radioactive isotope of lead (in this case, radium D) as the metal to be removed. One point on a quartz tube was blown out to a thin wall, and a small amount of the mixture of radium D, E, and F from old emanation tubes was placed in the tube opposite the thin spot. By heating the evacuated tube at this point, and simultaneously cooling the thin portion with water, a radioactive deposit, so slight as to be invisible, was formed on the thin wall. The vapor from a 1% solution of non-radioactive lead tetramethyl in octane was passed at 1–2 mm. pressure along the tube and into a liquid air trap. Light from a mercury arc equipped with a shutter was focused on the tube at a point from 10 to 30 cm. in advance of the radioactive deposit.

A β-ray electroscope was placed above the radioactive deposit, and the contents of the trap were also examined for β-activity. The latter was accomplished by distilling the liquid in the trap in

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(15) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); Paneth and Lautsch, *ibid.*, **64**, 2702 (1931).

order to remove any solid radioactive material which might have been carried over, then treating the distillate with excess bromine in carbon tetrachloride, evaporating in a vacuum, and testing the residue with a β-ray electroscope.

With the shutter closed, no change in β-activity could be observed in the tube, and no activity appeared in the trap. Upon opening the shutter and allowing ultraviolet radiation to reach the vapor, still no difference was observed in the tube, but β-activity appeared, with increasing intensity, in the trap. When the tube was heated instead of irradiated at a point some 10 cm. removed from the metal deposit, identical observations as to β-activity were made. The volatile radioactive product formed appeared on subsequent treatment to be inseparable from the unchanged lead tetramethyl frozen with it in the trap.

It may be concluded from this evidence that free methyl groups are produced during the photolysis of lead tetramethyl. Since the β-activity observed is that of radium E, the facts that no decrease in activity was observed in the tube, and that the activity in the trap increased on standing, indicate that radium D was carried over while radium E (a bismuth isotope) was not. Loss in β-activity in the tube due to removal of a portion of the radium D would be slow in appearing. No α-activity tests were made. These experiments could perhaps be carried out in more quantitative fashion by using thorium B rather than radium D, since thorium B and its immediate decomposition products have β-activities and half lives which would make possible direct and immediate observations of the rate of disappearance of the metal in the tube. Applications of the method to the study of free radical production in other photochemical reactions are obvious.

Summary

Continuous absorption in the ultraviolet, producing decomposition into metallic lead and hydrocarbons, has been observed for lead tetramethyl and tetraphenyl. The method of radioactive indicators has been applied to determine quantum yields for lead tetramethyl vapor and for both compounds in solution, and to show the formation of methyl radicals during the photolysis of lead tetramethyl vapor. Short chains, retarded by oxygen, are indicated in the vapor; deactivation or recombination reduces the quantum yield in solutions.

STANFORD UNIVERSITY, CALIF.

RECEIVED DECEMBER 16, 1935

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 521]

The Mercury-Photosensitized Decomposition of Arsine

BY NORWOOD L. SIMMONS AND ARNOLD O. BECKMAN

Introduction

The photochemical and mercury-photosensitized decompositions of ammonia have been studied by many investigators. The photo-decompositions of phosphine have also been studied[1] although reliable quantum yield data are still lacking. The present investigation is concerned with the mercury-photosensitized decomposition of the related compound arsine and the quantum yield for the reaction.

Cheesman and Emeléus[2] have reported that the photochemical decomposition of arsine results in the formation of hydrogen and a brown solid film which deposits on the walls of the reaction vessel and was assumed to be arsenic. Since the continuous absorption of arsine begins at 2390 Å., it is apparent that the sensitized decomposition by mercury atoms activated with 2537 Å. may be investigated without the occurrence of any direct photochemical decomposition.

Experimental Procedure

Arsine was prepared by the action of dilute sulfuric acid on an alloy of arsenic and zinc prepared according to the directions of Cohen.[3] The gaseous arsine was swept by a current of dry nitrogen through drying tubes containing calcium chloride and phosphorus pentoxide into a trap immersed in liquid air. The arsine was purified by repeated distillations *in vacuo* and was stored in a glass bulb at a pressure of about 200 mm. No thermal decomposition during storage was observed. The molecular weight of the gas, as determined by means of the quartz fiber gage attached to the system, agreed closely with the calculated value 77.95 for arsine.

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(1) Melville, *Proc. Roy. Soc.* (London), **A138**, 374 (1932); **A139**, 541 (1933).

(2) Cheesman and Emeléus, *J. Chem. Soc.*, 2847 (1932).

(3) Cohen, *Z. physik. Chem.*, **25**, 483 (1898).