

other instantaneously, for they are decomposed as soon as formed. If they do rearrange instantaneously, there would be no essential difference between numbers 2 and 3. In any event, the rearrangement takes place during or after the formation of the alkenyl metallic bromides, but before hydrolysis takes place.

Although the mechanisms of the transformations of crotyl and methylvinylcarbinyl bromides to butenes by the Grignard procedure and zinc in alcohol treatment need not necessarily be the same, nevertheless, the similarity in results by the two procedures indicates that this may be the case. The differences in results between the zinc and magnesium methods which are observed might well be due to differences in solvents, metals, and temperature. For example, the higher temperature of the zinc method yields a larger quantity of the *cis* compound than does the lower temperature of the Grignard method, as might be expected from the effect of temperature on *cis-trans* equilibria. The reactions of crotyl and methylvinylcarbinyl bromides with other metals are now being studied in several solvents.

It should be noted that the very reactions car-

ried out in this investigation were reported by Charon⁸ in 1899. Not realizing that he was actually working with a mixture of bromides, Charon treated so-called crotyl bromide with zinc in alcohol and reported a butene which gave a dibromobutane boiling at 158°. It happens that 158° is the exact boiling point of meso-2,3-dibromobutane, obtained from *trans*-2-butene. In fact, one of us, on the basis of Charon's report, at one time² attempted to synthesize pure *trans*-2-butene by this method. It is evident that Charon, not anticipating any rearrangements to give mixtures, neglected to mention the small boiling range which his dibromobutane must undoubtedly have had.

Summary

An allylic rearrangement to an equilibrium has been shown to occur when different mixtures of crotyl and methylvinylcarbinyl bromides are decomposed with zinc in alcohol to form butenes. The composition of the butene mixture obtained is 62.1 ± 1.9% 1-butene, 30.5 ± 0.5% *cis*-2-butene and 7.5 ± 2.4% *trans*-2-butene.

(8) Charon, *Ann. chim. phys.*, [7] 17, 197 (1899).

LOS ANGELES, CALIF. RECEIVED DECEMBER 12, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochemical Decomposition of Oxalyl Chloride Vapor

BY K. B. KRAUSKOFF AND G. K. ROLLEFSON

The existence of the intermediate COCl and its usefulness in explaining the mechanisms of various photochemical reactions involving phosgene have been amply demonstrated by previous investigations in this Laboratory.¹ Since the oxalyl chloride molecule consists of two COCl radicals joined through a C-C bond, its reaction should be related to those of phosgene, and it was hoped that a study of this substance would lead to further information concerning COCl. The first reaction selected for investigation was the photochemical decomposition of the vapor, which is reported in the present paper.

Apparatus and Materials

Oxalyl chloride was prepared by fractional distillation from a mixture of anhydrous oxalic acid and phosphorus pentachloride which had been allowed to stand for several

(1) See Montgomery and Rollefson [THIS JOURNAL, 56, 1089 (1934)] for bibliography.

days. The fraction distilling between 61 and 65° was placed in a liquid air trap and further purified by vacuum distillation, only about half the original quantity of material being kept.

Other gases used in these experiments, chlorine, phosgene, carbon monoxide and carbon dioxide, were prepared by orthodox methods.

The corrosive properties of oxalyl chloride necessitated special precautions for its handling and its preservation. No stopcock lubricant could be found immune to attack by its vapor. All ordinary greases, including Shell Apiezon, developed leaks after a few seconds' exposure. Phosphoric acid is useless because of its water content. The only material which proved at all satisfactory was a mixture of glycerol, mannitol and dextrin in the ratio 24:4:15 parts by weight. Even this mixture was slowly attacked, resulting in a gradual "freezing" of the stopcock; but it seldom developed leaks, and by frequent replacement could be made to serve fairly well. To protect the stopcock attached directly to the oxalyl chloride reservoir, the material was kept in a trap surrounded at all times by liquid air.

The photochemical decomposition of oxalyl chloride vapor results in an increase of pressure, so that the most

convenient method of measuring the reaction rate is by observation of the pressure change. The usual procedure for making such measurements, by connecting the reaction vessel directly to a liquid manometer, was unsuitable for these experiments because oxalyl chloride reacts with all of the common manometer liquids. Accordingly a click gage was employed, the outer surface of the gage connecting with a large manometer containing α -bromonaphthalene. Thus the reaction mixture was entirely enclosed by glass or quartz except for a single stopcock lubricated with the glycerin grease described above. α -Bromonaphthalene was selected as the manometer liquid because of the relatively low vapor pressure of oxalyl chloride at room temperature; the initial pressures used in these experiments varied from 15 to 100 cm. of α -bromonaphthalene.

Three different reaction vessels were used, one a cylindrical Pyrex vessel of about 200-cc. capacity, one a spherical quartz flask of 250-cc. capacity, and the third a cylindrical quartz vessel of about 40-cc. capacity. The quartz vessels were attached to the line by means of graded quartz-Pyrex seals.

The temperature coefficient of the reaction is very small, so accurate thermostating of the reaction vessel was not attempted. For part of the work the temperature was kept approximately constant by allowing tap water to trickle over the reaction vessel, and for the remainder the reaction vessel was exposed to the air between readings and immersed in water at 25° when the readings were taken.

The light source was a Cooper-Hewitt quartz mercury arc, provided with a cylindrical quartz lens and for most of the work placed within a few cm. of the reaction vessel. For runs in which it was desired to exclude radiation below 3000 Å., a Pyrex plate was placed in front of the arc; to isolate lines near 2537 Å. a quartz bulb filled with chlorine and bromine was used as a filter.

For the measurements of quantum yield a cylindrical quartz reaction vessel 10 cm. long, with plane ends, was placed lengthwise in the light path. Behind it was placed a surface thermopile connected to a sensitive galvanometer. To isolate the 2537 line the chlorine-bromine filter described above was used, together with a nickel sulfate-cobalt sulfate solution. To isolate the 3650 line, a Corning red-purple filter (No. 587) and a copper ammonium sulfate solution were used.

Absorption coefficients were measured with the aid of a Hilger quartz spectrograph and a Zeiss microphotometer. The absorption cell was a quartz tube 19.6 cm. long with plane windows and a side-tube into which the oxalyl chloride could be frozen when necessary.

Results and Discussion

In order to obtain reproducible rate measurements, it was necessary to freeze the gas for each run after it was admitted into the reaction vessel, evacuate the reaction vessel thoroughly with a mercury diffusion pump, and then distil off a little of the substance as it warmed up. Even with these precautions strict reproducibility was not attained, but the variations from run to run were usually slight. Probably the lack of repro-

ducibility can be traced to impurities introduced by a slight reaction of the vapor with the stopcock grease in passing from the reservoir to the reaction vessel.

When the precautions just mentioned are observed, oxalyl chloride shows no tendency to decompose thermally at room temperature. The vapor absorbs radiation of all wave lengths below about 3800 Å., and is slowly decomposed by light of any wave length in this region. The reaction is approximately first order (*cf.* Figs. 1 and 2) with respect to light absorbed, and yields phosgene and carbon monoxide as its principal products. The total pressure at the end of the reaction is a little more than twice as great as the initial pressure, the excess indicating a slight decomposition of the phosgene formed.

That phosgene and carbon monoxide are the chief reaction products was confirmed by pressure measurements taken at different times during the reaction while the reaction vessel was immersed in liquid oxygen. The amount of non-condensable gas found in these experiments always corresponded with the observed pressure change. To prove that the excess pressure observed at the end of the reaction was due to phosgene decomposition, mixtures of phosgene and carbon monoxide were introduced into the reaction vessel and illuminated under similar conditions; the pressure changes observed were of the same magnitude as the discrepancies in the final pressure readings for the oxalyl chloride runs.

Although the reaction is predominantly first order, plots of $\log(a-x)$ against time show some deviations from linearity (Fig. 1). During the first few minutes of reaction these curves always show a slight decrease in slope; thereafter the slope may increase or decrease somewhat, depending on the type of illumination employed. In Fig. 1, the middle curve represents illumination with the full light of the mercury arc; the upper two are typical of runs illuminated with a Pyrex plate interposed, *i. e.*, principally with the lines near 3130, 3340 and 3650 Å.; and the two lower ones are examples of runs illuminated through a chlorine-bromine filter, *i. e.*, chiefly with the 2537 Å. line. Scales of both abscissas and ordinate on this graph are different for the different curves, in order to bring out their differences in shape more clearly. The two upper curves show a tendency for the unimolecular k_s to grow smaller as the reaction proceeds; the other three

have an opposite deviation, the change in slope being greatest for the runs illuminated through the chlorine-bromine filter.²

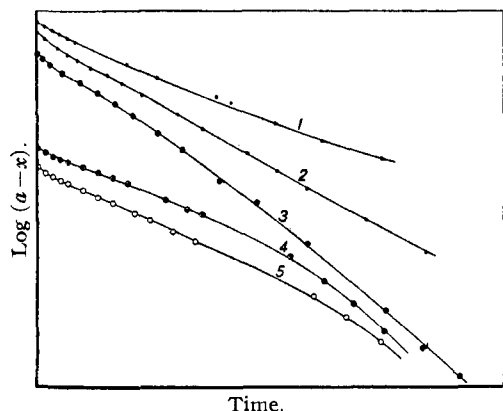


Fig. 1.—Curve 1.—Initial pressure = 55.0 cm. Pyrex reaction vessel. Curve 2.—Initial pressure = 48.0 cm. Quartz reaction vessel with Pyrex plate before arc. Curve 3.—Initial pressure = 46.4 cm. Full arc illumination. Curve 4.—Initial pressure = 46.7 cm. Chlorine-bromine filter. Curve 5.—Initial pressure = 25.6 cm. Chlorine-bromine filter.

In an attempt to find an explanation for these changes of the rate curve with wave length, the quantum yield of the reaction was measured for the lines 3650 and 2537 Å. These measurements were carried out in the usual manner, using a surface thermopile and filters for isolating the desired wave lengths. The light absorption was so small, even with relatively high pressures of oxalyl chloride, that accuracy in the measurements was impossible to obtain. Since the pressure changes used in the measurements were those at the beginning of the reaction where the rate is slightly greater than normal, the results may be a little high. The following values for the quantum yield were obtained.

3650 Å.:	2.2	1.5	1.6	Av. 1.8
2537 Å.:	0.6	0.7	1.1	Av. 0.8

In spite of the inaccuracy of these values, it is certain that the quantum yield is very small, probably in the neighborhood of one for low wave lengths and two for higher wave lengths.

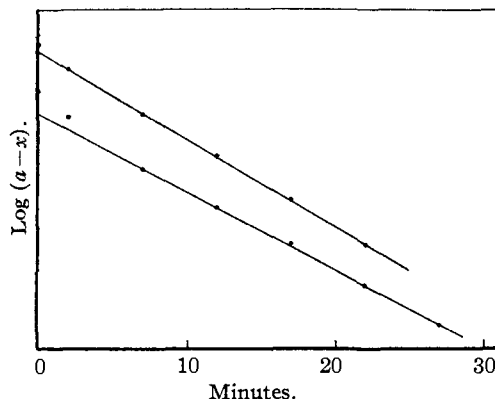
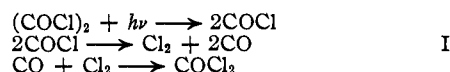
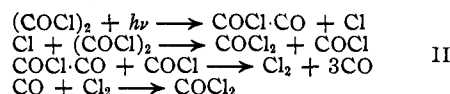


Fig. 2.—Vertical scale the same for both curves, but displaced somewhat to separate the curves. Upper curve, pressure $(\text{COCl})_2 = 40.4$, pressure $\text{CO} = 41.3$ cm. Lower curve, pressure $(\text{COCl})_2 = 42.1$ cm.

Various mechanisms can be set up to account for these quantum yields. The following pair appear reasonable, and offer satisfactory explanations for most of the data obtained for the reaction



at low wave lengths; and



at high wave lengths. Of course these mechanisms are not considered as mutually exclusive; one is simply supposed to predominate in one region of the spectrum, the other in another region. Both mechanisms give unimolecular rate laws, and are capable of accounting for the deviations from linearity shown in Fig. 1. When the reaction is proceeding by mechanism I, any process which produces chlorine atoms—*e. g.*, side reactions such as spontaneous decomposition of the unstable COCl , or photochemical decomposition of phosgene—would enable the second step of mechanism II to take place. This would increase the quantum yield and so cause an apparent rise in the unimolecular constant, especially in the latter part of the reaction, as is shown by

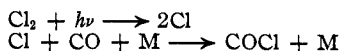
(2) A perplexing phenomenon associated with the initial stages of the reaction is the almost invariable appearance in the reaction vessel of a faint mist composed of minute but clearly visible droplets or particles. When illumination is commenced, the reaction vessel, at first clear, shows a faint cloudiness which in a minute or so (sometimes longer) resolves itself into a mass of tiny droplets circulating with the heat currents developed by the arc. The mist appears only in the light-path, and is not visible when the light is turned off. It gradually disappears as the reaction goes toward completion, becoming invisible when 40–60% of the oxalyl chloride is used up. A careful study of the initial part of the reaction has failed to give any information regarding the origin or composition of the mist. Temperature, wave length of illumination, changes in stopcock lubricant, produce no observable effect upon it. The pressure during the first minute of reaction shows a perfectly steady increase, without a sign of the sudden decrease which condensation of an intermediate would necessitate. Since the mist apparently produces no appreciable effect on the course of the reaction, it was considered safe to disregard it.

the shape of the three lower curves in Fig. 1. If the reaction occurs according to mechanism II, any process which removes Cl, such as $\text{CO} + \text{Cl} + \text{M} \rightarrow \text{COCl} + \text{M}$, will lower the quantum yield. This decrease in the yield should become more marked as the concentration of carbon monoxide increases, and so should cause the apparent falling off in the unimolecular k 's illustrated by the two upper curves in Fig. 1.

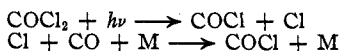
In both of the mechanisms it is assumed that chlorine is one of the initial products of decomposition of oxalyl chloride, and that phosgene is formed by a subsequent reaction. To avoid complicating the above reaction schemes unduly, the mechanism of phosgene formation is not shown. It must take place through a reaction



The necessary COCl may come from the reactions



when long wave length illumination is used, or from the reactions



at short wave lengths, or in part from the reactions in mechanisms I and II.

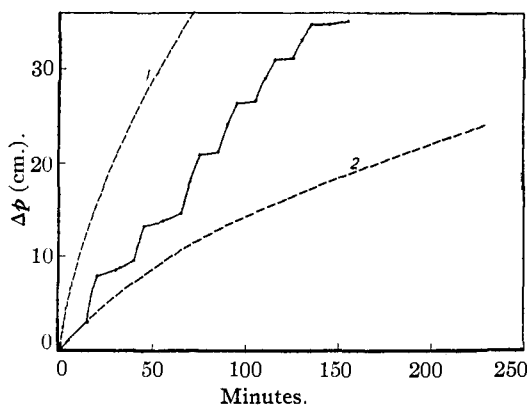


Fig. 3.—Initial pressure = 48.0 cm.; illumination alternately with and without Pyrex plate before arc. Dotted curves 1 and 2 represent rate curves for the same initial pressure, with continuous full arc illumination and continuous illumination through Pyrex, respectively.

The assumption that chlorine is the initial product of decomposition explains two experimental facts very satisfactorily. One of these is the steep slope always observed at the beginning of the logarithmic curves. The formation of chlorine and carbon monoxide from oxalyl chloride gives a greater pressure change than the formation of

phosgene; hence Δp at first will be relatively high, and will fall off as the concentrations of carbon monoxide and chlorine become appreciable. In the later stages of the reaction the balance between the decomposition of oxalyl chloride and the formation of phosgene will keep the rate fairly uniform. The well-known susceptibility of the phosgene reaction to inhibition by traces of impurities may partially account for the difficulty in obtaining reproducible runs.

The second observation which makes necessary the assumption that chlorine is a primary product of dissociation is the almost complete elimination of the steep portion of the logarithmic curve when the reaction takes place in the presence of excess carbon monoxide (Fig. 2). The added carbon monoxide speeds up the formation of phosgene as soon as any chlorine is produced, and so allows the reaction to attain its "normal" rate sooner than it can ordinarily. Except for this effect at the beginning of the reaction, the only influence of carbon monoxide on the decomposition of oxalyl chloride is a slight retardation when it is added in large excess. Large amounts of phosgene and carbon dioxide added initially produce a similar but somewhat smaller retardation.

Differences in the degree of completeness of the phosgene reaction at different wave lengths are rather strikingly shown by runs such as that illustrated in Fig. 3, in which oxalyl chloride was illuminated alternately with and without a Pyrex plate interposed before the arc. The dotted lines above and below the reaction curve are drawn in for comparison from other runs; Curve 1 shows the reaction rate which would have been observed if illumination without the Pyrex plate had been continuous, and Curve 2 shows the rate curve which would have resulted from continuous illumination with the plate in position. After a period of illumination through Pyrex the formation of phosgene is practically complete, since phosgene absorbs no radiation above 3000 Å., and consequently when the plate is removed the rate of pressure increase should at first be greater than normal because of dissociation of the phosgene. Thus the steep portions of the reaction curve have greater initial slopes than the normal slopes for corresponding pressures indicated by Curve 1. On the other hand, when illumination through Pyrex follows a period of full arc illumination, the formation of phosgene cuts down for a time the apparent rate of pressure increase. Accordingly,

the less steeply inclined portions of the reaction curve have initial slopes considerably smaller than those indicated by Curve 2.

For a unimolecular reaction, initial rates should vary directly as initial pressures. Initial rates for the oxalyl chloride decomposition, however, show a marked falling off from this proportionality, the amount of falling off being highest when illumination is limited to lines near 2537 Å. These facts are illustrated by Curves 1, 2 and 3 of Fig. 4, showing the variation of initial rate with pressure for illumination through Pyrex, illumination with the full arc, and illumination through the chlorine-bromine filter, respectively. Different time intervals were selected in measuring the initial rates for the three curves, in order to make their differences in curvature more apparent.

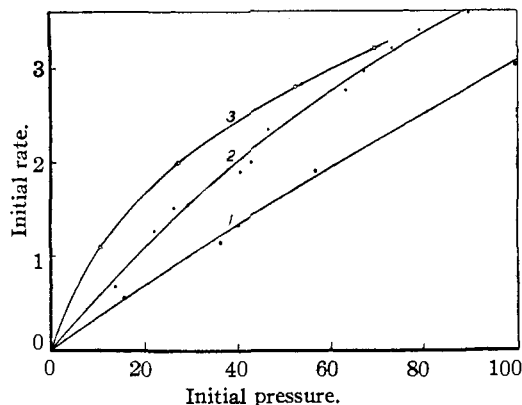


Fig. 4.—Curve 1.—Illumination through Pyrex plate. Curve 2.—Full arc illumination. Curve 3.—Illumination through chlorine-bromine filter.

The initial rates might still be proportional to light absorbed in accordance with the unimolecular law if the absorption coefficient of oxalyl chloride is relatively high and if it increases rapidly with decreasing wave length of the absorbed light. Values of the absorption coefficient necessary to account for the curves of Fig. 4 can be calculated easily by assuming that the reaction rate is proportional to I_{abs} , and then expressing I_{abs} in terms of the absorption coefficient

$$r = kI_{\text{abs}} = kI_0(l - I/I_0) = kI_0(l - 10^{-\epsilon p})$$

I_0 is incident light, I is light transmitted, ϵ is the absorption coefficient, l is the average length of the light path through the reaction vessel (2.7 cm.) and p is the pressure in cm. of α -bromonaphthalene. The values of ϵ calculated in this manner are 0.0005, 0.0015 and 0.007, respectively, for the three curves.

To test this explanation for the shape of the curves in Fig. 4, direct measurements were made of the absorption coefficients of oxalyl chloride for eleven wave lengths between 2400 and 3700 Å. The measurements were carried out with an apparatus and a technique exactly similar to those described in an earlier paper by Montgomery and Rollefson,³ and the details need not be repeated here. Eight spectrograph plates were taken, using different pressures of the vapor and different exposure times; on some of the plates four faint bands are observable in the absorption spectrum: 3460, 3300, 3150 and 3020 Å. Using the photometer curves made from these plates, values of ϵ were calculated by means of the formula $\epsilon = (1/p)l \log_{10}(I_0/I)$, in which the symbols have the same meaning as above (here $l = 19.6$ cm.). The results ($\epsilon \times 10^3$) are shown in the accompanying table and graphically in Fig. 5.

Plate no.	II	III	IV	V	VI	VII	VIII
Pressure	76.4	46.2	46.4	24.0	24.0	14.1	14.1
3700 Å.	0.03						
3602	.06						
3450	.17		0.17				
3302	.24		.23				
3194	.24	0.24	.23				
3036	.30	.26	.28				
2883		.32		0.32			
2756		.44		.41			
2618					0.68	0.61	
2492					.87		0.91
2392							.99

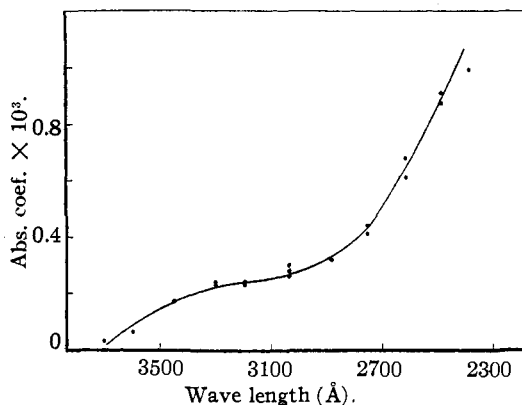


Fig. 5.—Absorption coefficients of oxalyl chloride.

From Fig. 5 a rough estimate can be made of the average absorption coefficients for the spectral regions involved when the reaction vessel is illuminated through Pyrex, with the full arc, and through the chlorine-bromine filter. These values are 0.0002, 0.0005 and 0.0008, respectively,

(3) Montgomery and Rollefson, THIS JOURNAL, 55, 4025 (1933).

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 il-

luminated 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 Tetraphenyl¹

BY PHILIP A. LEIGHTON AND RAYMOND A. MORTENSEN

The discovery by Midgley and Boyd² 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 Terenin⁵ and of Duncan and Murray⁵ 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;

(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).