

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## Two Reactions of Gaseous Methyl and Ethyl

BY J. H. SIMONS AND MALCOLM F. DULL

The free existence in the gas phase of the methyl and ethyl radicals has been postulated frequently in the past to explain certain gaseous reactions of carbon compounds. Paneth and his co-workers<sup>1</sup> have assumed these same particles in order to explain the removal of lead, antimony and zinc mirrors by the transitory decomposition products of lead alkyls. Rice<sup>2</sup> has made the same assumption in his discussion of the thermal decomposition of hydrocarbons.

Although the existence of short-lived chemically active molecular species in the thermal decomposition of carbon compounds has been established, the identification of these as free radicals (odd molecules) is still open to question. Other assumptions have been made such as the one of Burk<sup>3</sup> that they are "hot" or activated molecules, and the suggestion of Kassel<sup>4</sup> that they are alkylidene radicals formed when two hydrogen atoms attached to the same carbon atom split off and form a hydrogen molecule.

The chemical reactions of these active particles were discussed by Rice<sup>2</sup> in regard to the thermal decomposition of hydrocarbons and by Simons, McNamee and Hurd<sup>5</sup> in the thermal decomposition of lead tetramethyl. Paneth and his co-workers<sup>1</sup> found that they would react with the metals lead, antimony, zinc, cadmium and tellurium; and Rice, Johnston and Evering<sup>6</sup> found that they would react with mercury but not with copper, iron or nickel and that these last three metals did not deactivate them. They do not react with glass or quartz; and the fact that the presence of oxygen prevents their action on mirrors of lead, antimony, cadmium and zinc indicates that they do not react with the oxides of these metals. Gilman and Brown<sup>7</sup> were unable to obtain beryllium diethyl by the action of the ethyl particles on a beryllium mirror.

A study of the chemical reactions of these particles is important in order to investigate their nature and may aid in obtaining more information about the mechanism of many reactions. The products of their reactions on antimony, zinc, cadmium and lead are complex and difficult to separate and identify, so these reactions are unsuited for their study. With mercury they form dialkyls, which on subsequent reaction with mercuric bromide

(1) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); Paneth and Lautsch, *ibid.*, **64**, 2702 (1931); Paneth and Herzfeld, *Z. Electrochem.*, **37**, 577 (1931).

(2) Rice, *THIS JOURNAL*, **53**, 1959 (1931).

(3) Burk, *J. Phys. Chem.*, **35**, 2446 (1931).

(4) Kassel, *Chem. Rev.*, **10**, 18 (1932); "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., 1932, p. 233.

(5) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

(6) Rice, Johnston and Evering, *THIS JOURNAL*, **54**, 3529 (1932).

(7) Gilman and Brown, *Rec. trav. chim.*, **50**, 184 (1930).

form alkyl mercuric bromides which can be identified readily. In this paper we are reporting two additional reactions, which also promise to be of use in the study of these particles.

These reactions are with an alkali metal and with a halogen. Sodium was the metal used and the formation of the very reactive sodium alkyls was established by causing them to react with ethyl alcohol and identifying the hydrocarbon. None of the elementary halogens have sufficiently low enough vapor pressures to be used as such, for the particles are deactivated by low temperatures. We therefore used iodine held in combination in carbon tetraiodide and identified the alkyl iodides from their crystalline addition products with quinoline.

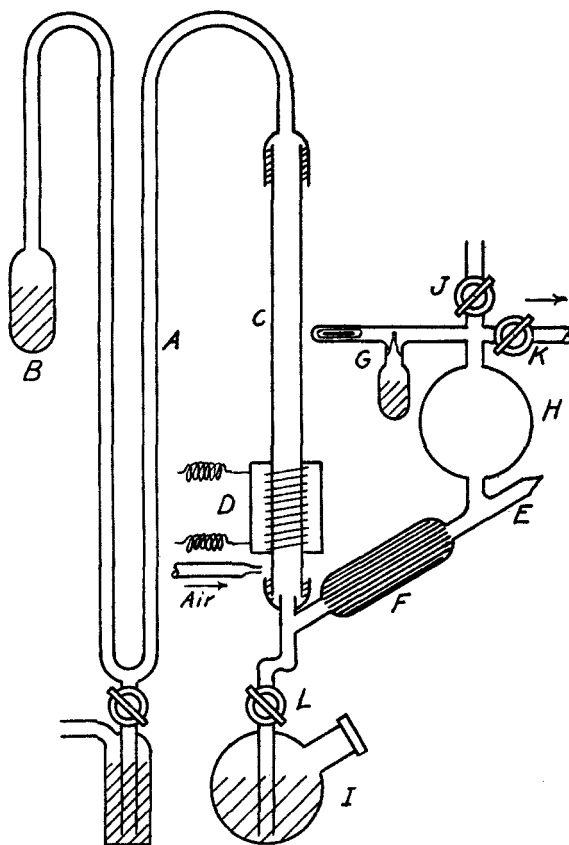


Fig. 1.

### Apparatus

The apparatus for the experiments with sodium (Fig. 1) was connected to the usual vacuum pump system. This contained a mercury vapor pump especially designed for speed. A mercury shut-off (A) was used to close the reservoir (B) containing the lead alkyl in order to eliminate the use of a stopcock with its grease. The quartz tube (C)

was sealed in the system with de Khotinsky cement or ordinary sealing wax. The furnace (D) was placed as near to the lower joint as was possible without softening the cement, which was cooled by a stream of air. Molten sodium (0.4–0.7 g.) was introduced

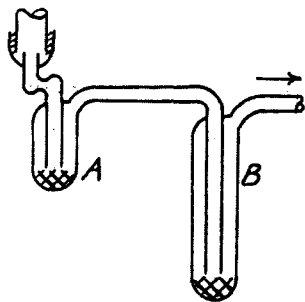


Fig. 2.

through the side tube (E) in an atmosphere of dry carbon dioxide and then distilled, after the system had been evacuated, into (F) which was filled with small glass rods. After a run, ethyl alcohol in the bulb (G) was introduced into the evacuated system by breaking the capillary separating it from the rest of the system with a glass enclosed nail moved by an electromagnet. The resulting gases were collected in the bulb (H) and withdrawn through stopcock (J) by introducing the mercury, alcohol or saturated salt solution contained in the flask (I).

For the experiments with carbon tetraiodide the same general set-up was used except that between the furnace and the pumps the apparatus shown in Fig. 2

was substituted. The trap (A) contained the carbon tetraiodide, and the resulting alkyl iodides were condensed in the trap (B) which contained quinoline and was cooled with liquid air.

### Experimental Procedure

**Preparation of Materials.**—Lead tetramethyl was prepared from methylmagnesium iodide and anhydrous lead chloride by the method of Calingaert.<sup>8</sup> The product, which boiled at 48–50° at 100 mm. pressure, was allowed to stand over freshly precipitated silver oxide for a week in order to remove residual iodides. It was dried over anhydrous calcium chloride and redistilled.

Lead tetraethyl of a commercial variety was purified in the above manner and redistilled.

Carbon tetraiodide was prepared from calcium iodide and carbon tetrachloride by the method of Spindler,<sup>9</sup> and purified by drying in vacuum over sulfuric acid and by sublimation in vacuum.

**Experiments with Sodium.**—After the sodium was introduced and distributed, the apparatus was evacuated, and the furnace adjusted to a temperature of about 900°. The bulb containing the lead alkyl was surrounded by a cooling mixture of ice and hydrochloric acid or ice and salt, depending on whether the substance in question was lead tetramethyl or lead tetraethyl. The mercury shut-off was then opened. The products of the decomposition of the lead alkyl passed directly through the chamber (F) containing a considerable surface of sodium. At the conclusion of the experiment, which required from seventy to ninety hours, the mercury shut-off was closed, and the system again exhausted for several hours. The furnace was allowed to cool, and the stopcock (K) closed. About 1.5–2.0 cc. of dry ethyl alcohol was introduced from (G). When the reaction with the sodium, which had acquired a dull gray color during the run, appeared to have ceased, the stopcock (L) was opened and mercury, alcohol or a saturated salt solution admitted from the reservoir (I). Most of the gas was thus trapped in the bulb (H). It was withdrawn through the stopcock (J) into a Hempel gas pipet preliminary to being transferred to an analytical apparatus.

The pressure during a run was in the range of 0.01 to 0.03 mm. of mercury, and no carrier gas was used.

**Experiments with Carbon Tetraiodide.**—The procedure in the experiments with

(8) Calingaert, *Chem. Rev.*, **2**, 55 (1925).

(9) Spindler, *Ann.*, **231**, 264 (1885).

carbon tetraiodide was very much the same as that used in those with sodium. The products from the decomposition of the lead alkyls came in contact with crystalline carbon tetraiodide in the trap (A), Fig. 2, which was immersed in an ice-bath. The trap (B) containing a few drops of redistilled quinoline was immersed in liquid air to condense gaseous products. At the conclusion of the run, which occupied twenty-four to thirty hours, the trap (B) was allowed to come to room temperature while the apparatus remained evacuated. It was then opened and the crystalline material in it was purified by recrystallization from anhydrous ethyl alcohol.

**Identification of Products.**—The gaseous products obtained in the experiments with sodium were analyzed in a modified Orsat apparatus. They were found to consist entirely of mixtures of hydrogen and hydrocarbon with traces of alcohol vapor readily removed by concentrated sulfuric acid. The composition was determined by combustion methods. The hydrogen was removed by passing the gas through a heated copper oxide combustion chamber and the hydrocarbon determined by burning a mixture of the gas with oxygen in a combustion pipet. As the total volume of gas obtained was known, the total amount of hydrocarbon produced in an experiment was easily calculated. The crystalline addition products of the alkyl iodides and the quinoline were identified by their melting points.

### Results

The results of the experiments with sodium are shown in Table I. Within the precision of the experiments methane is the only hydrocarbon formed after the reaction with alcohol when lead tetramethyl is used, and ethane when lead tetraethyl is used. This indicates that sodium methyl is formed by the reaction of the active particles with sodium in the first case; and sodium ethyl, in the second.

TABLE I  
EXPERIMENTS WITH SODIUM

Lead alkyl.....	Tetramethyl	Tetraethyl	
Time of run, hours.....	90	70	83
Wt. of sodium, g. approx.....	0.7	0.7	0.4
Vol. of gas obtained, cc.....	378	479	255
Temperature ( <i>T</i> ), °C.....	20	19	22
Pressure ( <i>P</i> ), mm.....	746	751	750
Analysis			
Vol. of sample, cc.....	99.5	98.6	99.5
Vol. CO <sub>2</sub> formed, cc.....	3.6	2.71	1.5
Contraction in combustion, cc.....	6.6	4.9	1.8
No. of C atoms = $\frac{3 \times \text{Vol. CO}_2}{2 \times \text{Contra.-Vol. CO}_2}$	1.1	1.1	2.1
Formula of hydrocarbon.....	CH <sub>4</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
Percentage hydrocarbon in gas.....	3.62	2.75	0.76
Total vol. hydrocarbon at <i>T</i> and <i>P</i> , cc.....	13.7	13.2	1.92

In Table II the results of the experiments with carbon tetraiodide are shown. These indicate in a similar manner that methyl iodide is formed by the reaction of the active particles from the thermal decomposition of lead tetramethyl with carbon tetraiodide and ethyl iodide by the active particles from lead tetraethyl. Not only was the melting point of the

quinoline methiodide determined and found to agree with that of a known sample, but the melting point of the hydrate obtained by crystallizing the substance from 95% alcohol was found and also a mixed melting point of this with the known hydrate.

TABLE II  
EXPERIMENTS WITH CARBON TETRAIODIDE

Lead alkyl.....	Tetramethyl	Tetraethyl
Time of run, hours.....	24	30
Wt. of quinoline addition product, g.....	0.10	0.23
M. p. from anhydrous $C_2H_5OH$ , °C.....	132-134	155-156
M. p. known quinoline methiodide, °C.....	135	
M. p. known quinoline ethiodide, °C.....		157
M. p. from 95% $C_2H_5OH$ , °C.....	70-71	
M. p. known quinoline methiodide-7H <sub>2</sub> O, °C.....	71.5-72	
Mixed m. p. known and suspected hydrates, °C.....	69.5-70	

The results obtained could not have been caused by a reaction of lead alkyl vapor with the reagents, for they were never permitted to come in contact with it. The vapors were not run through the apparatus when the furnace was cold, and when it was hot they were completely decomposed, as is shown from the fact that there was no condensation in the liquid air trap, although five grams of the lead alkyls were run through the apparatus.

In addition the following two experiments were performed.

Sodium was placed in contact with lead tetramethyl in an evacuated sealed tube for several months. There was no apparent reaction. An analysis of the gas formed, when the contents of the tube were dissolved in alcohol, showed it to be pure hydrogen.

In a similar experiment with carbon tetraiodide the bright red color of the substance persisted for several weeks. It then slowly faded to an orange color. After several months the tube was opened and quinoline introduced. Crystalline quinoline methiodide was formed. This indicates that there is a reaction between carbon tetraiodide and lead tetramethyl, but that it is probably a slow one. In our runs the same reaction did not take place, for the color of the carbon tetraiodide did not change.

### Discussion

These experiments demonstrate the great range of chemical activity of the transitory alkyl particles with reactions with an alkali metal on the one hand and a halogen on the other. The reaction with carbon tetraiodide is an argument against the assumption of Kassel that the active particles are alkylidene radicals, for in that case diiodomethane and diiodoethane should be formed in the experiments. The two reactions may be used as an argument, but not a conclusive one, against the assumption that the active particles are ions. If they were negative ions, we should expect

the reaction with the metals to take place much more readily than with the halogens; and, if positive ions, we should expect the reverse.

As these experiments were performed without the use of a carrier gas, as has been used almost exclusively by previous investigators, and at a much lower total pressure, it is established that the active particles can be formed under these conditions.

### Summary

Two new reactions of the transitory ethyl and methyl fragments formed in the thermal decomposition of lead tetraethyl and lead tetramethyl have been investigated.

They have been found to react with elementary sodium to form sodium ethyl and sodium methyl.

They have been found to react with carbon tetraiodide to form ethyl iodide and methyl iodide.

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## The Absorption and Fluorescence Spectra of the Acid Sulfates of Quinine and Ten of its Derivatives in Water and Aqueous Sulfuric Acid Solution

BY LAWRENCE J. HEIDT AND GEORGE S. FORBES

The main purpose of this investigation was to determine accurately the absorption spectra of the bisulfates of quinine and its derivatives used by us in earlier work.<sup>1,2,3</sup> For comparison with that work, half our measurements were carried out in 0.9 molar sulfuric acid. In such a solution the loss of hydrogen ion due to the photochemical reaction can be neglected, as well as the accompanying change in the molar extinction coefficient,  $K$ , of the reactants.<sup>1</sup> Previous workers have plotted absorption curves of the acid salts of several of these compounds,<sup>4</sup> but little attention has been given to the effects of changing the groups attached to the quinoline nucleus particularly at positions four and six. Also the range of acidity covered has been small. That such effects do occur has been suggested by values of  $K$  determined throughout the spectrum for quinine<sup>2</sup> and at isolated wave lengths for the other compounds.<sup>3</sup>

The fluorescence spectra of these compounds was also studied to account for the low quantum yield (around 0.07) of the photochemical reaction with

(1) Forbes, Heidt and Boissonnas, *THIS JOURNAL*, **54**, 960 (1932).

(2) Forbes, Heidt and Brackett, *ibid.*, **55**, 588 (1933).

(3) Forbes and Heidt, *ibid.*, **55**, 2407 (1933).

(4) For data and a review of the literature see Hicks, *Australian J. Exptl. Biol. Med. Sci.*, **7**, 171 (1930).