Notes

Note on an Improved Laboratory Ozonizer

By Lee Irvin Smith and Glenn E. Ullyot

Some years ago one of us[1] published a description of a convenient laboratory ozonizer capable of giving high concentrations of ozone. Recently the original ozonizer was rebuilt and simplified, and since requests for details regarding the machine have come to us frequently, we are publishing a short description of the new machine.

The new tubes have the same dimensions as the old ones, except that the upper collar (Fig. 1, Ref. 1, p. 1845) marked "litharge cement" instead of being 2.7 cm. is about 10 cm. high, and the inner core and the mercury filling have been dispensed with. This collar carries a cork stopper, through which passes a short piece of glass tubing, and the copper wire from the secondary of the transformer passes through this piece of tubing and reaches nearly to the bottom of the ozonizing tube. The inner tube is filled with distilled water, the three ozonizing tubes are connected in series through mercury seals and the whole assembly set in the large battery jar which then is filled with distilled water. During operation, the temperature of the water in the inner tube rises a few degrees in the course of two or three hours, but the temperature of the outer bath of water remains practically constant even when the machine is run continuously for long periods of time.

We first tried making the new tubes of thin-walled Pyrex glass, but to our astonishment, these tubes sparked continuously and gave almost no "silent discharge," with the result that very little ozone was produced. We tried reducing the voltage in the primary of the transformer, and also changing the distance between the inner and outer tubes, but in all our experiments one of two things invariably happened: either no current at all passed, or else there was sparking, and in none of our experiments with Pyrex were we able to get more than about 2% ozone. We therefore returned to soft glass as the material out of which to construct the tubes.

The general assembly, details of analysis, procedure, etc., were the same as those described in the original paper. Using three tubes in series, 0.055 Kva transformer wound 88 to 1 and taking 110 volts in the primary, the new machine, with dry oxygen, gives from 4.5 to 7.0% ozone by volume (6.7 to 10.0% by weight) when the gas is passing at rates of 19 and 6.5 liters per hour, respectively.

Finally, we have eliminated the hot tube ozone "destroyer" used in connection with the older work, because, when using inflammable solvents, the exit gases occasionally became ignited in the destroyer and struck back into the reaction apparatus. If the exit gases are passed through two

(1) Smith, This Journal, **47**, 1844 (1925).

towers filled with broken glass and moistened with 5% sodium hydroxide solution, practically all the ozone is destroyed, and this is a much safer way of destroying the excess ozone than the hot tube–manganese dioxide method previously used.

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The Thermal Decomposition of Lead Tetraphenyl

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The quantitative production of diphenyl from lead tetraphenyl has been reported by Zartman and Adkins.[1] They state that both the presence of nickel as a catalyst and hydrogen at high pressure (100 atmospheres) were necessary in this reaction at 200°. We have found, however, that a quantitative yield of diphenyl could be obtained at a somewhat higher temperature, 252°, and in the absence of hydrogen or other gas and without the addition of catalyst.

We have studied the thermal decomposition of lead tetraphenyl over a range of temperature in sealed Pyrex bulbs, which were carefully evacuated after the introduction of the lead tetraphenyl. The technique was similar to that used by Simons, McNamee and Hurd[2] in their work on the static decomposition of lead tetramethyl.

The lead tetraphenyl used had been prepared in the usual way from phenylmagnesium bromide and lead chloride and purified by crystallization from hot benzene. It was a white crystalline substance with a melting point of 223°.

The data which we have obtained are given in the table of results. The yield of diphenyl is smaller as the temperature used is higher, and benzene and *p*-diphenylbenzene are both formed at the higher temperatures.

TABLE OF RESULTS

Run number	1	2	5	6	7	3	4
Temperature, °C.	252	345	400	400	450	450–460	550
Time, minutes	135	130	60	80	45	30	20
Sample, g.	2.1	2.0	3.0	3.0	3.0	2.0	2.0
Lead tetraphenyl recov., g.	0.0	0.1	0.19	0.22	0.24	0.68	...
Lead tetraphenyl dec., g.	2.1	1.9	2.81	2.78	2.76	1.32	...
Benzene obtained, g.	0.0	..	0.39	0.40	0.21	...	...
p-Diphenylbenzene obtained, g.	0.0	0.57	.13	.16	.05	...	...
Diphenyl obtained, g	1.3	.57	.77	.47	.37	...	...
Yield of diphenyl, %	100	50	46	28	22	...	...

(1) Zartman and Adkins, THIS JOURNAL, **54**, 3398 (1932).
(2) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

Remarks.—Unpurified diphenyl from run 1 had a melting point of 69–69.5°. The temperature of 252° was the lowest at which observable decomposition took place. The lead deposit in run 1 was bright. All other runs exhibited more or less charring. In runs 2 and 6 the bulb was placed in the cold furnace and then rapidly heated. In the other runs the bulb was placed in a hot furnace. The benzene was determined by the difference in weight caused by passing a stream of air through the bulb. These values are probably high, due to the volatility of diphenyl. The undecomposed lead tetraphenyl was recovered by precipitation with acetone, and the *p*-diphenylbenzene and diphenyl separated by solution in ethyl alcohol.

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COMMUNICATIONS TO THE EDITOR

THE FREE METHYLENE RADICAL

Sir:

We have been decomposing diazomethane in a current of ether since some time, in attempts to isolate the methylene radical. Blank runs showed that ether alone, under the conditions of our experiments, does not decompose appreciably under 750°. Using the ether–diazomethane mixture and combining the fragments with metallic mercury [see Rice, Johnston and Evering, THIS JOURNAL, **54,** 3529 (1932)] we obtained no trace of any organic compound of mercury with the furnace below 650°, although a considerable portion of the diazomethane decomposed, and antimony mirrors could be readily removed at furnace temperatures as low as 450°. A run at 700° gave an appreciable yield of an organo-mercury compound which was identified as dimethylmercury by adding iodine to the contents of the liquid air trap after distilling off the undecomposed diazomethane; in this way we obtained pure methylmercuric iodide, CH_3HgI, identified by its mixed melting point.

It seems reasonable to infer from these experiments that, if the CH_2 group has been formed, it does not combine with mercury to form $Hg=CH_2$, since the addition of iodine to this compound should give CH_2IHgI. Furthermore, it seems very probable that at temperatures of 700° and higher, the methylene group picks off a hydrogen atom from one of the surrounding ether molecules, thus producing a free methyl group.