chlorocarbonate in a small amount of ether was added dropwise to a solution of 22.4 g. (0.08 mole) of 1-benzyl-4-aminomethyl-4-phenylpiperidine (IV) in 100 ml. of pyridine at room temperature; a solid settled out. The mixture was kept at room temperature for sixteen hours and then at 60° for one hour; this heating caused the solid to dissolve; on cooling 13 g. of crystallized solid of m. p. 228–229° was obtained, as well as an additional 9 g. (m. p. 225–227°) by precipitation with ether; total yield was 22 g., 71%. Recrystallization from alcohol-ether raised the m. p. to 232–233° dec.

Acknowledgment.—The authors wish to acknowledge, with appreciation, the advice of Dr. C. M. Suter and Dr. J. S. Buck. We wish to thank Dr. T. J. Becker for the pharmacological data and the Misses Bass, Raney and Curran for the microanalyses recorded.

Summary

A series of amines and diamines in the 4-phenylpiperidine series have been prepared. The ureido, guanidino and urethan derivatives of these various amines have been synthesized. Straight chain analogs of several piperidine derivatives have been prepared. The compounds described in this paper have been submitted for pharmacological assay and many of them were found to show a mild spasmolytic but negative analgesic action.

RENSSELAER, N. Y. RECEIVED MAY 21, 1947

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Ignition of *n*-Butane by the Spontaneous Oxidation of Zinc Dimethyl[1]

BY ELMER J. BADIN, DAVID R. WALTERS AND ROBERT N. PEASE

It is well known that zinc dimethyl inflames spontaneously in air or oxygen at room temperature. This fact suggests that zinc dimethyl oxidation might be used to ignite a hydrocarbon such as *n*-butane. Our experiments show that this can be accomplished.

The oxidation of zinc dimethyl vapor has been previously studied by Thompson and Kelland[1a] and Bamford and Newitt.[2] At room temperature there is a fast but non-explosive reaction at pressures of a few millimeters of mercury. This reaction gives rise to a white mist which consists of a solid of approximate composition $2[(CH_3)_2Zn]\cdot O_2$, as judged by the pressure decrease, and the ratio of zinc dimethyl and oxygen consumed. No appreciable amounts of gaseous products are detected.

With an increase of pressure there is a transition to explosion after an induction period of several seconds. As in the slow reaction the white mist is first formed. Explosion is accompanied by a very brilliant white flash when oxygen is in excess, shading off to a less brilliant blue-green color at intermediate compositions. With an excess of zinc dimethyl the flash is fainter and reddish, in some cases visible only in a darkened room. A solid deposit forms on the reaction vessel walls which varies from grey-white to black, sometimes appearing as a bright metallic mirror.

We have repeated some of this work, and have in addition studied the induced oxidation of *n*-butane.

Experimental

Reactions were carried out in spherical Pyrex bulbs of 6.6 cm. diameter. Before each experiment, a bulb was washed with boiling nitric acid, rinsed with distilled water, dried for fourteen hours or more at 135° and then blown out with dry air. Bulbs were connected to the apparatus by a ground glass joint, and were thermostated at 20°.

The apparatus was of conventional design, including the reaction bulb, a bulb for liquid zinc dimethyl, a mercury manometer, and Langmuir and Hyvac pumps. After evacuation, zinc dimethyl vapor was admitted to the desired pressure. Dry oxygen (or air) was then introduced as quickly as possible from a reservoir previously adjusted to the proper pressure. When *n*-butane was to be included, it was admitted after the zinc dimethyl. No reaction occurred between the two.

Stopcocks and the ground glass joint were lubricated with Apiezon grease. No reaction between the grease and zinc dimethyl was apparent.

When the gaseous products were to be analyzed, samples were withdrawn by means of a modified Töpler pump. They were analyzed by absorption in 30% aqueous potassium hydroxide (carbon dioxide), bromine water (olefins), Oxsorbent (oxygen), Cosorbent (carbon monoxide). Hydrogen was determined by combustion over copper oxide at 310°, and paraffins at 570°.

Zinc dimethyl was prepared from methyl iodide and zinc dust containing 5% cupric oxide, which was reduced in hydrogen before use. Last traces of methyl iodide were removed by treating with anhydrous silver oxide followed by fractionation in a 20-plate column (nitrogen atmosphere). This point received special attention since preliminary experiments indicated some inhibition by methyl iodide.

Results and Discussion

A set of data for the non-explosive reaction are given in Table I. Runs with foreign gases present are included.

A white mist appeared immediately on adding oxygen, though there was a short induction period with the rate passing through a maximum (Fig. 1). The pressure decreased quite rapidly to a value roughly equivalent to a loss of 1 to 1.5 times the zinc dimethyl present. Gas analysis revealed no gaseous products. Thus the result is consistent with the assumption that the solid product is equivalent to 2 molecules or more of zinc dimethyl to 1 molecule of oxygen.

---

[1] The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University. Acknowledgment is also due to Dean Hugh S. Taylor, who has general supervision of this project.

[1a] Thompson and Kelland, *J. Chem. Soc.*, 746 (1932).

[2] Bamford and Newitt, *ibid.*, 695 (1946).

TABLE I

TRANSITION FROM SLOW TO EXPLOSIVE OXIDATION OF ZINC DIMETHYL

(Temp., 20°)

Initial reactant pressures, mm. $(CH_3)_2$-Zn	O_2	Added gas	Total ΔP, mm.	Max. rate, mm./sec.	Fractional rate, sec.$^{-1}$	Fractional rate / $[(CH_3)_2Zn]$
20 Vol. % $(CH_3)_2Zn$						
4	16	..	− 5	0.04	0.0080	0.0020
8	32	..	−11	.10	.0091	.0011
12	48	..	−15	.41	.027	.0023
14	56	..	−19	Expl. 9 sec.		
10 Vol. % $(CH_3)_2Zn$						
8	72	..	−11	0.30	.027	.0034
10	90	..	−14.5	.41	.028	.0028
12	108	..	−17.5	.82	.047	.0039
13	117	..	−24	Expl. 12.6 sec.		
5 Vol. % $(CH_3)_2Zn$						
7.5	142.5	..	−10	0.20	.030	.0040
13.5	256.5	..	−20	.68	.034	.0025
14.5	275.5	..	−22	Expl. 12.6 sec.		
20 Vol. % $(CH_3)_2Zn$ (nitrogen present)						
12	10	38	−14	0.22	.016	.0013
14	11.8	44.2	−17	.41	.024	.0017
16	13.4	50.6	−21	.56	.027	.0017
20 Vol. % $(CH_3)_2Zn$ (helium present)						
14	11.2	44.8	−11	0.17	.015	.0011
16	12.8	51.2	−16	.28	.018	.0011
18	14.4	57.6	−18	.45	.025	.0014
19	15.2	60.8	..	Expl.		
20 Vol. % $(CH_3)_2Zn$ (*n*-butane present)						
18	240	52	−15	0.38	.025	.0031
10	240	50	−17	.46	.027	.0027
12	240	48	−20	.80	.040	.0033
14	240	46	+26	Expl.		

Earlier workers write the product as zinc methyl methoxide (CH_3–Zn–OCH_3). This was the conclusion of Frankland,[3] and of Butlerow[4] when air or oxygen was passed through a solution of zinc dimethyl in an inert solvent. We can only say that zinc dimethyl vapor and oxygen condense in the ratio of 2:1 or more to give a solid. This might legitimately be regarded as a sort of addition co-polymer, with the understanding that the solid will certainly adsorb a portion of any excess of the relatively involatile zinc dimethyl (b. p. + 46°). It is not improbable that the oxygen is present originally as an –O–O– peroxide grouping.

In order to obtain a rough idea of the kinetics of the process, the maximum rates (inflection points) were compared with the total pressure change, and with the initial pressures of reactants. Rates are known only approximately because the reaction is so rapid. Nevertheless it appears that the fractional rate (maximum rate divided by total pressure change) tends to increase with the zinc dimethyl pressure, roughly independent of oxygen pressure. Substitution of nitrogen or helium for a part of the oxygen depresses the rate somewhat, helium being much more effective than nitrogen. The last column in Table I contains the calculated ratio—fractional rate divided by the zinc dimethyl concentration. This ratio is roughly constant in each series, indicating a second-order overall dependence on zinc dimethyl concentration, with some disturbance due to oxygen and added gases.

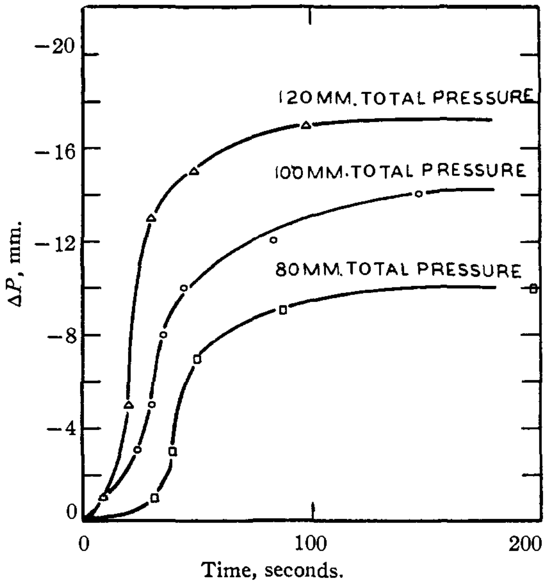

Fig. 1.—Slow oxidation of zinc dimethyl: 10% zinc dimethyl in oxygen, 20° (explosion limit 125 mm.).

When the maximum rate approached 1 mm. per second, the mixture exploded. This usually occurred at about 15 mm. of zinc dimethyl pressure over a fairly wide concentration ratio, as may be seen in Tables I and II.

TABLE II

EXPLOSIVE OXIDATION LIMITS FOR ZINC DIMETHYL-OXYGEN MIXTURES

Initial temperature 20.0°, clean Pyrex surface, 6.6 cm. bulb.

Total pressure, mm.	$[(CH_3)_2Zn]$, mm.	$[O_2]$, mm.
280	14	266
125	13	112
65	13	52
35	14	21
25	15	10

Composition of the gaseous products after explosion is given in Table III. It will be noted that now there are substantial quantities of such products as carbon dioxide, carbon monoxide and hydrogen, whereas in the non-explosive region the amounts are negligible. Even so, the pressure change may still be negative.

With *n*-butane present, the minimum partial pressure of zinc dimethyl required for explosion is

---

(3) Frankland, *Ann.*, **85**, 347 (1853).

(4) Butlerow, *Z. pharm. Chem.*, **7**, 402 (1864).

TABLE III

PRODUCTS FROM THE OXIDATION OF ZINC DIMETHYL IN THE EXPLOSIVE REGION

Initial temperature, 20°

Reactants: Pressure zinc dimethyl, mm.	Reactants: Pressure oxygen, mm.	Change in pressure after explosion, mm.	Gaseous products volume %: % CO_2	% CO	% O_2	% H_2	% CH_4
30	170	−69	43	1	44	12	0
50	150	..	19	22	37	19	3
80	120	..	4	30	21	42	3
120	80	..	2	31	14	22	30

still in the neighborhood of 15 mm. as the last entry in Table I shows. Because of the violence of the explosion, it was necessary to limit the total pressure. A set of runs at 200 mm. total pressure, with a constant partial pressure of 25 mm. zinc dimethyl (well above the minimum required) and varying proportions of butane and oxygen, is given in Table IV. Gas analyses were carried out and the results converted to partial pressures after explosion. (These data do not include condensible products such as water.)

TABLE IV

OXIDATION OF *n*-BUTANE WITH ZINC DIMETHYL IGNITION

200 mm. total pressure, 20°

Initial pressure, mm.: $(CH_3)_2Zn$	*n*-C_4H_{10}	O_2	Total pressure change, mm.	Composition after explosion, mm.: O_2	CO_2	CO	H_2	Olef.	Paraf.
25	0	175	− 82	90	27	1	...	..	..
25	10	165	− 79	22	64	6	29	..	..
25	20	155	− 63	10	8	74	44	..	..
25	35	140	+185	8	4	181	193	..	..
25	50	125	+172	15	0	156	182	15	4
25	95	80	+ 53	25	0	91	96	18	23

These data clearly indicate that the oxidation of butane may be induced by the ignition of the zinc dimethyl, though the precise mechanism is in doubt. No other induced combustions by metal alkyls have been reported. The studies of Taylor and co-workers[5] and Frey[6] have shown that methyl radicals from decomposing metal alkyls can set up a chain reaction to induce "cracking" reactions with hydrocarbons, such reactions occurring at significantly lower temperatures than in the absence of radicals from the metal alkyls.

One may speculate that when the rate of formation of the solid product of zinc dimethyl oxidation becomes sufficiently high, such free radicals as CH_3, CH_3O and CH_3OO are liberated. These radicals then set up a chain in the zinc dimethyl–butane–oxygen mixture, with self-heating and explosion as a result. Attempts at a material balance make it clear that condensable liquid products are also present. The nature of these will require further investigation.

Acknowledgment.—The authors wish to acknowledge the assistance of Stanley S. Weiss in preparative work.

Summary

1. The oxidation of zinc dimethyl with oxygen in clean Pyrex bulbs has been studied. The effect of nitrogen, helium and *n*-butane as inerts on the slow oxidation have been determined.

2. It has been shown that the ignition of a hydrocarbon, *n*-butane, may be initiated by the explosive zinc dimethyl oxidation at room temperature.

(5) See, *e. g.*, H. S. Taylor and Jones, THIS JOURNAL, **52**, 1111 (1932); Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

(6) Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).

PRINCETON, NEW JERSEY RECEIVED APRIL 30, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC, PHYSICAL AND CATALYTIC CHEMISTRY OF THE INSTITUTE OF CHEMISTRY AND AGRICULTURE "NICOLAOS CANELLOPOULOS," ATHENS AND PIRAEUS, GREECE]

Reactions of Iron Pyrite: Its Thermal Decomposition, Reduction by Hydrogen and Air Oxidation

BY GEORGE-MARIA SCHWAB AND JOHN PHILINIS

The thermal reduction of pyrite is said to begin at about 500°[1–5] and proceeds according to the equation

$$FeS_2 \longrightarrow FeS + 1/n\ S_n \qquad (1)$$

However, previous studies[1–9] have been rather fragmentary and consequently little is known of the actual mechanism by which the decomposition occurs. To this end detailed investigations of the kinetics of the decomposition, which has been found to proceed with a conveniently measurable velocity in the range 600–650°, have been carried out.

The reduction with hydrogen takes place at a somewhat lower temperature, 500°, according to the equation

$$FeS_2 + H_2 \longrightarrow FeS + H_2S \qquad (2)$$

further reduction to metallic iron occurring only above 900°.[7,10] Studies on the unknown kinetics

(1) G. Marchall, *Bull. soc. chim.*, [4] **35**, 43 (1924).

(2) L. d'Or, *Compt. rend.*, **190**, 1296 (1930).

(3) L. d'Or, *J. chim. phys.*, **28**, 377 (1931).

(4) I. N. Issakow, *J. Applied Chem.* (U. S. S. R.), **12**, 388 (1939); *Chem. Zentr.*, **111**, I, 2773 (1940).

(5) W. S. Udinzewa and G. I. Tschufarow, *J. Applied Chem.* (U. S. S. R.), **14**, 3 (1941); *Chem. Zentr.*, **112**, II, 863 (1941).

(6) A. F. Gill, *Can. J. Research*, **10**, 703 (1934).

(7) G. Gallo, *Ann. chim. applicata*, **17**, 39 (1927).

(8) R. Juza and W. Biltz, *Z. anorg. allgem. Chem.*, **205**, 273 (1932).

(9) J. A. Hedvall and R. Hedin, *Die Chemie*, **56**, 45 (1943).

(10) F. C. Thompson and N. Tilling, *J. Soc. Chem. Ind.*, **43**, T37 (1923).