[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Oxidation of Butene-1 Induced by Aluminum Borohydride*

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In connection with a general program on the induced combustion of hydrocarbons, studies of the action of zinc dimethyl,[1] boron triethyl,[2] and nickel carbonyl[3] have been previously reported. This paper deals with a similar investigation using aluminum borohydride, $Al(BH_4)_3$. Most of the data refer to the combustion of butene-1, but some observations on *n*-butane, propane and butadiene-1,3 are also given.

Experimental

The apparatus used has previously been described.[1] Spherical reaction bulbs were of 6.6 cm. inside diameter, and were cleaned by treatment with boiling concentrated nitric acid followed by thorough rinsing with distilled water. Drying was carried out overnight in an oven at 135°. A clean reaction bulb was used for each experiment.

In carrying out an experiment, aluminum borohydride was measured into the evacuated reaction bulb. The hydrocarbon was then admitted to a reservoir in an amount sufficient to give the desired pressure of hydrocarbon plus aluminum borohydride when the connecting stopcock between reservoir and reaction flask was opened. The reaction flask was then shut off, the reservoir flask evacuated and used to add oxygen in the same manner. The stopcock was quickly opened wide to induce thorough mixing of the gases. Gases were admitted to the reaction bulb from above. Both the reservoir and reaction bulb were thermostatted at 20°. Pressures were read on a mercury manometer, and a McLeod gage calibrated for the range 0.01–15.00 mm.

Gas samples were analyzed for carbon dioxide (30% aqueous potassium hydroxide), olefins (Lusorbent), oxygen (Oxsorbent), carbon monoxide (Cosorbent), hydrogen (combustion over cupric oxide at 310°), and paraffins (combustion over cupric oxide at 570°).

Aluminum borohydride was used as supplied by The Naval Research Laboratory and the Ethyl Corporation. It was attached to the apparatus by a mercury cut-off valve and a stopcock lubricated with Apiezon grease.

Oxygen was obtained from the American Oxygen Company; hydrocarbons from the Matheson Company. Oxygen was dried by means of phosphorous pentoxide, the hydrocarbons by Drierite.

Results and Discussion

It had been previously found that aluminum borohydride does not react with *dry* oxygen over a range of compositions and pressures at 20°.[4] It was therefore not too surprising to find that *n*-butane was not affected under conditions which had led to combustion with the sensitizers previously employed.[1,2,3] On the other hand, with moist oxygen, explosion of aluminum borohydride had been found to occur at 20°; and as might be expected, the combustion of added hydrocarbon is then induced. For example, in one series of experiments with propane it was established that a mixture containing 21 mm. of C_3H_8, 5 mm. of $Al(BH_4)_3$ and 23 mm. of O_2 would explode if the water vapor content exceeded about 0.6 mm. Explosion occurred at once or not at all; in no case was an induction period observed.

In contrast with the conclusions regarding the water vapor requirement in the combustion of aluminum borohydride and added saturated hydrocarbons, it was subsequently found that the unsaturated hydrocarbons, butene-1 and butadiene-1,3, could explode in the presence of aluminum borohydride even with *dry* oxygen. A more detailed study of the behavior of butene-1 was then carried out. This forms the subject of the present report.

Mixtures of butene-1, aluminum borohydride, and dry oxygen explode over a range of compositions and pressures at 20° after an induction period which may run to 400–500 seconds.[5] Some of the data are presented in Table I. In the first of the two series the partial pressure of $Al(BH_4)_3$ was maintained at 5 mm., while the proportions of C_4H_8-1 and O_2 were varied, keeping the total pressure at 100 mm. Explosion took place over a wide range; mixtures containing from 3.2 to 84.2% butene-1 ignited, although in runs containing large amounts of butene-1 combustion was very incomplete.

For these experiments flashes were a very brilliant green with a small amount of butene-1, white at intermediate compositions, a dull orange at high percentages of butene-1, and almost invisible for very large amounts of butene-1. Corresponding to these colors, the solid residues were white for the brilliant flashes, black to brown for orange flashes, and when incomplete combustion occurred, a very small amount of white residue formed.

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(1) Badin, Walters and Pease, THIS JOURNAL, **69**, 2586 (1947).
(2) Brokaw, Badin and Pease, *ibid.*, **70**, 1921 (1948).
(3) Badin, Hunter and Pease, *ibid.*, **70**, 2055 (1948).
(4) Badin, Hunter and Pease, *ibid.*, **71**, 2950 (1949).
(5) With butadiene-1,3 reaction was instantaneous in many instances.

TABLE I

INDUCED COMBUSTION OF BUTENE-1 WITH $Al(BH_4)_3$

100 mm. total pressure, 20°

Reactants pressure, mm.			Induction period, sec.	ΔP, mm.	Gaseous products, mm.					
$Al(BH_4)_3$	C_4H_8	O_2			CO_2	Olef.	O_2	CO	H_2	Paraf.
			$Al(BH_4)_3$ constant, C_4H_8/O_2 varied							
5.0	1.3	93.7	No flash in 1200 sec.							
4.9	3.0	92.1	455	− 18.6	3	1	70	1	7	1
5.0	9.9	85.1	105	− 36.3	38	4	7	3	8	4
5.1	20.3	74.6	100	+ 50	12	6	4	54	63	11
5.0	30.0	65.0	85	+127	2	2	1	100	122	2
5.1	40.1	54.8	76	+ 91	6	14	4	59	95	12
5.0	52.6	42.4	58	+ 65	4	30	9	39	56	25
5.0	61.0	34.0	240	+ 41	4	38	5	23	36	34
5.0	70.8	24.2	75	0	2	53	12	4	15	13
5.0	80.0	15.0	83	− 3	3	60	3	1	19	11
5.1	90.3	4.6	No flash, gradual pressure drop							
			Over-all Composition: $[Al(BH_4)_3 + 3O_2] + [C_4H_8 + 2O_2]$							
0.55	32.2	67.3	No reaction in 1200 sec.							
.70	32.6	66.7	No reaction in 1200 sec.							
.87	31.9	67.2	No reaction in 3000 sec.							
.93	31.6	67.5	268	+111	2	12	6	89	99	3
.93	33.2	65.9	3	+134	2	25	5	85	111	5
1.05	31.8	67.2	2	+ 97	..	..	..	...	...	..
3.0	29.3	67.7	1	+112	..	..	..	...	...	..
3.5	28.6	67.9	1	+114	..	..	..	...	...	..
4.0	28.0	68.0	75	+123	2	17	2	80	118	4
4.9	26.7	68.8	80	+119	2	19	4	72	117	5
7.6	22.3	70.1	79	+ 86	4	4	3	73	101	2
10.0	20.2	69.8	82	+104	1	17	3	55	122	6
10.1	19.7	70.2	116	+ 73	2	12	4	51	97	7
12.5	17.3	70.2	138	+ 59	3	1	3	50	106	1
15.3	13.0	71.7	Slow reaction with gradual pressure drop							

Combustion products on the lean side were primarily CO_2 and water. On increasing the richness of the mixtures, CO and H_2 became the principal constituents and, finally, with extremely rich mixtures large amounts of unreacted olefin were found.

In the second series of Table I the amount of $Al(BH_4)_3$ was varied, the over-all composition corresponding to $(Al(BH_4)_3 + 3O_2)$ plus $(C_4H_8 + 2O_2)$. These compositions were arbitrarily chosen as being of constant "richness" to give CO and H_2 as gaseous reaction products. Explosion occurred within limits of 0.93 to 12.5 mm. of $Al(BH_4)_3$. As anticipated, the products were predominantly hydrogen and carbon monoxide; in most cases these gases accounted for more than 85% of the gaseous products, the ratio of H_2 to CO increasing, in general, as the amount of aluminum borohydride increased. The additional observation was made that with low concentrations of aluminum borohydride the visible flash was orange and with high concentrations, a bright green. Further, although the induction period increased with increasing $Al(BH_4)_3$ pressure, the explosion with high concentrations of aluminum borohydride was more violent.

Finally, the explosion pressure limits were obtained for mixtures of composition corresponding to those of the second part of Table I, but at varying total pressure. Determinations were made at 75, 100, 120, 140, 150, 170 and 200 mm. total pressure. The data for 100 mm. total pressure are contained in the second series of Table I, from which the limit is interpolated (0.90 mm. of $Al(BH_4)_3$). Similar data for other total pressures are contained in Table II. Experiment numbers are given to indicate the order in which runs were made. Also letters indicate the flask in which each experiment was performed. In the experiments in the vicinity of the limit, particularly at higher pressures, a mist was formed suddenly anywhere up to 50 seconds after the gases were mixed. If explosion were to take place, it followed the mist formation immediately. Otherwise, no flash resulted. The explosion limits interpolated from the data in Table II and the second part of Table I are shown in Table III and in Fig. 1.

Attention is called to the cusp in the explosion limit curve. Thus in the combustion of a mixture containing 0.9% aluminum borohydride, three limits are observed: a lower limit at 100 mm. total pressure, an upper limit at 139 mm., and a third limit at 157 mm. total pressure. This phenomenon of lower and upper limits is characteristic of chain

TABLE II

DETERMINATION OF THE EFFECT OF TOTAL PRESSURE ON THE EXPLOSION LIMITS OF MIXTURES OF $[Al(BH_4)_3 + 3O_2] + [C_4H_8 + 2O_2]$

Run	Flask	Reactants pressure, mm. $Al(BH_4)_3$	C_4H_8	O_2	Induction period, sec.	ΔP, mm.	Remarks
75 mm. Total Pressure							
36	J	3.5	19.7	51.8	560	+ 30	Bright green flash
37	L	3.0	21.2	50.8	485	+ 55	Bright green flash
39	A	2.5	21.7	50.8	140	+ 79	Bright green flash
38	F	2.0	22.5	50.5	...	...	No flash in 2000 sec.
100 mm. Total Pressure: See second part of Table I							
120 mm. Total Pressure							
57	E	1.06	39.9	79.0	3	...	Orange flash
59	P	0.96	38.7	80.3	2	+ 46	Sooty orange flash
58	J	0.93	38.7	80.4	...	...	No flash in 1300 sec.
56	A	0.87	39.0	80.1	...	...	No flash in 1300 sec.
140 mm. Total Pressure							
60	B	1.48	45.5	93.0	37	+186	Orange flash
64	C	1.39	44.9	93.7	2	+178	Orange flash
61	D	1.29	44.9	93.8	2	...	Orange flash
63	Q	1.27	45.0	93.7	...	...	No flash in 1650 sec.
62	H	1.08	45.1	93.8	...	...	No flash in 1000 sec.
150 mm. Total Pressure							
46	G	1.66	48.0	100.3	130	+214	Orange flash
48	F	1.60	47.9	100.5	45	+212	Orange flash
67	J	1.56	47.9	100.5	1	+186	Orange flash
68	D	1.52	48.0	100.5	55	+209	Faint orange flash
49	D	1.48	8.0	100.5	...	...	No flash in 1000 sec.
69	B	1.46	48.1	100.4	...	...	No flash in 1500 sec.
47	M	1.42	48.1	100.5	...	...	No flash in 2300 sec.
170 mm. Total Pressure							
65	L	1.41	54.9	113.7	22	+239	Orange flash
66	F	1.33	54.9	113.8	...	...	No flash in 1000 sec.
200 mm. Total Pressure							
50	B	1.69	62.7	135.6	2	+278	Orange flash
51	Q	1.52	64.5	134.0	2	+247	Orange flash
54	C	1.47	63.8	134.7	1	+171	Orange flash
55	E	1.42	64.8	133.8	...	...	No flash in 1000 sec.
53	J	1.37	64.7	133.9	...	...	No flash in 1100 sec.
52	L	1.15	65.8	133.0	...	...	No flash in 1000 sec.

TABLE III

EXPLOSION LIMITS FOR THE INDUCED COMBUSTION OF BUTENE-1 WITH ALUMINUM BOROHYDRIDE[a]

(Temperature, 20°)

Total pressure, mm.	$Al(BH_4)_3$ limit pressure, mm.	% of total pressure	Pressure, mm. Butene-1	Oxygen
200	1.44	0.72	64.7	133.9
170	1.37	0.81	54.8	113.8
150	1.51	1.00	49.5	100.5
140	1.28	0.91	45.0	93.9
120	0.94	0.79	38.7	80.4
100	0.90	0.90	32.1	67.0
75	2.2	3.00	22.1	50.7

[a] Composition of mixtures corresponds to $[Al(BH_4)_3 + 3O_2] + [C_4H_8 + 2O_2]$.

activation and deactivation with change of pressure. The phenomenon of a lower and upper limit first observed by Semenoff[6] for phosphorus and oxygen has since been observed by many other investigators for a variety of oxidation systems. Dijksman and co-workers[7] have observed a result for spark ignition of hydrogen–oxygen mixtures similar to that shown in Fig. 1.

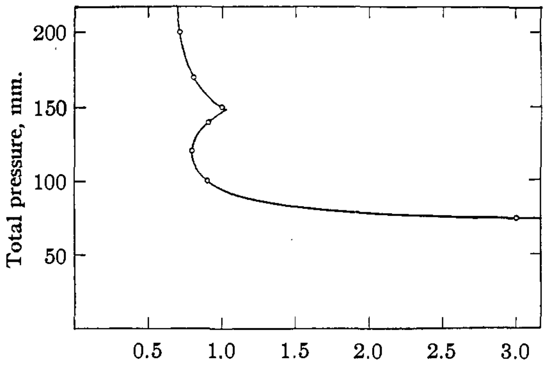

Fig. 1.—Explosion limits for aluminum borohydride–butene-1–oxygen mixtures: clean pyrex surface; bulb diameter, 6.6 cm.; temperature, 20°.

One further observation may be added. As noted in Table I, a slow pressure drop was observed outside the explosion region. Since no such effect occurs in the absence of butene (that is, with dry oxygen alone), a direct interaction of butene and borohydride is indicated. A detailed study of this reaction has accordingly been undertaken and will be reported later. The interaction takes place readily at somewhat higher temperatures (50–70°) possibly with the formation of alkyl derivatives. This is presumed to be the primary reaction upon which the over-all oxidation in dry oxygen depends.

Summary

1. For the induced combustion of C_4 hydrocarbons with aluminum borohydride in dry oxygen, *n*-butane gave no explosion, butene-1 exploded after an induction period, and butadiene-1,3 yielded immediate explosion.

2. A study of the induced combustion of butene-1 has been carried out. The limits and effect of total pressure for the reaction have been determined, and an upper and lower limit has been observed.

3. There is evidence of initial reaction between butene and borohydride as the starting mechanism.

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(6) Semenoff, *Z. Physik*, **46**, 109 (1927).

(7) Dijksman, *Rec. trav. chim.*, **57**, 1059 (1938); **59**, 857 (1940); Dijksman and van den Brandhof, *ibid.*, **59**, 445 (1940).