tures of the spectrum[9] may be analyzed on the basis of the following band types: (I) 0–0, (II) $0 - \nu$, (III) $0 + \nu'$, (IV) $0 + \nu_i' + \nu_j'$, (V) $0 + 2\nu'$, (VI) $0 - \nu_L$, (VII) $0 + \nu_L'$, (VIII) $0 + \nu' + \nu_L'$, (IX) $0 + \nu' - \nu_L$. Here ν is a ground state fundamental; ν' is an excited state fundamental; ν_L and ν_L' are rather intense low frequency bands. Table IV gives the particular ν, ν', ν_L and ν_L' values used in this analysis.

TABLE IV

Raman and infrared[a]	This research ν	ν_L	ν_L'	ν'
240	244	7	59	746
510	514	43	107	948
622	621	86	148	959
777	774	102		1209
999	1001			

[a] Pitzer, Guttman and Westrum, THIS JOURNAL, 68, 2209 (1946).

Five fundamentals appearing in type II bands are correlated with the Raman and infrared data. In the excited state the four fundamentals (III) are assigned on the basis of position, intensity and appearance in combinations of type (IV). The prominent excited state frequencies at 1694, 1705, 1907, 1955, 2157 and 2168 (see Fig. 4) are accounted for in this manner. The relatively strong band at 0 + 940 is not assigned to a fundamental because it fails to combine with the 746 and 1208. Instead, it is taken as arising from a type (IX) combination in which ν_L is 7. It should be noted that no band in the 500 cm.$^{-1}$ region is of sufficient intensity to test as a fundamental. The significance of this is discussed in a previous section. With reasonable allowances for anharmonicity, assignments are made for type (VI) for each of the fundamentals.

One feature of the spectrum is the appearance of many low frequency bands, some of which combine with the fundamentals. These may be rotation bands, difference frequencies, or excited state low frequency fundamentals. Because of the lack of a basis for sorting out their origin, those which combine are grouped with the subscript L. All those listed in Table IV, combine in forms (VIII) and (IX).

Summary

The vapor and solution spectra of phenylisopropane, phenylcyclohexane, phenylcyclopentane, phenylcyclopropane, phenylacetylene and styrene are presented. From them, it is concluded that the cyclopentyl and cyclopropyl groups exhibit ring strain and that the long wave length spectrum of styrene is a monosubstituted benzene spectrum. A vibrational analysis of the styrene spectrum is also given.

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[9] A total of some 402 bands were measured. The complete table together with the specific assignments may be obtained in mimeographed form upon request.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Effect of Traces of Oxygen on the Reaction of Aluminum Borohydride with Ethylene[1]

BY RICHARD S. BROKAW AND ROBERT N. PEASE

In studying the induced combustion of hydrocarbon–oxygen mixtures with aluminum borohydride[2] it was found that only with unsaturated hydrocarbons did explosion occur in the absence of water vapor. This led to a study of the reaction between olefins and aluminum borohydride.[3] The kinetics of this reaction were determined; the reaction is first order with respect to the aluminum borohydride concentration and zero order with respect to the olefin. It was shown that boron alkyls are among the reaction products.

The object of the research described in this paper has been to investigate the effect of oxygen on the reaction between aluminum borohydride and ethylene.

Experimental

The apparatus used for the kinetic studies has previously been described.[3] As before, spherical reaction bulbs were of 6.6 cm. inside diameter. It was found necessary to seal a clean reaction flask to the apparatus for each experiment. Aluminum borohydride was obtained from the Naval Research Laboratory and ethylene from U. S. Industrial Chemicals, Inc.

Experiments were carried out in the same manner as those in the absence of oxygen,[3] except that small amounts of oxygen (measured with a McLeod gage) were premixed with the ethylene.

A few explosion limit experiments were performed. For this purpose the apparatus was altered to the type used by Badin, Walters and Pease[4] in studying the ignition of n-butane with zinc dimethyl. Experiments were performed in the same fashion as in the induced combustion of butene-1.[2]

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(1) (a) Taken from a thesis submitted by Richard S. Brokaw in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. (b) 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; and Contract N6-ori-105 with the Office of Naval Research and Office of Air Research as coördinated by Project Squid, Princeton University. (c) We wish to acknowledge the assistance of Dean H. S. Taylor, who has general supervision of this project. (d) Reproduction in whole or in part permitted for any purpose of the United States Government.

(2) Brokaw, Badin and Pease, THIS JOURNAL, 72, 1793 (1950).

(3) Brokaw and Pease, *ibid.*, 72, 3237 (1950).

(4) Badin, Walters and Pease, *ibid.*, 69, 2586 (1947).

Results and Discussion

Some typical pressure–time curves for the aluminum borohydride–ethylene reaction under a variety of conditions are illustrated in Fig. 1. Curve 1, which is almost linear, is typical of the reaction in the absence of oxygen, and the kinetics have previously been elucidated.[3] Curves 2 and 3 illustrate the striking effect of traces of oxygen on the reaction rate. First there is an induction period during which the reaction proceeds at a rate comparable to that observed in the absence of oxygen. Next a large increase in rate is observed which falls off rapidly, however, and finally approaches the velocities found with aluminum borohydride and ethylene alone. "Curve breaks" such as those observed in the reaction without oxygen,[3] and attributable to the exhaustion of the ethylene, were also noted.

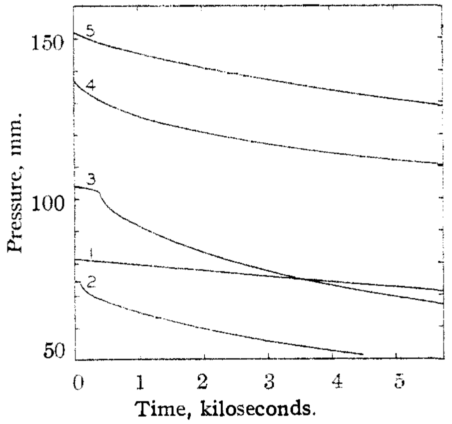

Fig. 1.—Pressure–time curves for various reaction mixtures at 49.9°: 1, 43.3 mm. $Al(BH_4)_3$, 38.0 mm. C_2H_4; 2, 38.7 mm. $Al(BH_4)_3$, 35.5 mm. C_2H_4, 0.33 mm. O_2; 3, 52.4 mm. $Al(BH_4)_3$, 51.2 mm. C_2H_4, 0.48 mm. O_2; 4, 49.1 mm. $Al(BH_4)_3$, 62.4 mm. C_2H_4, 0.31 mm. O_2, 25.6 mm. $B(C_2H_5)_3$; 5, 62.7 mm. $Al(BH_4)_3$, 64.4 mm. C_2H_4, 0.27 mm. O_2, 12.3 mm. $B(C_2H_5)_3$, 12.3 mm. $Al(BH_4)_2C_2H_5$.

Assuming that the products of the reaction and the stoichiometry are the same, as given in equation (1)

$$Al(BH_4)_3 + 4C_2H_4 \longrightarrow B(C_2H_5)_3 + Al(BH_4)_2C_2H_5 \quad (1)$$

it is possible to calculate the concentrations of reactants and products from the total pressure at any time. (Bear in mind that the evidence for the product $Al(BH_4)_2C_2H_5$ is indirect,[3] and its existence has not been established with certainty.) The shape of the curves suggests that perhaps the reaction products serve to inhibit the effect of the added oxygen, so that the rate observed in the absence of oxygen is approached asymptotically. The following equation was assumed to describe the reaction

$$-\frac{1}{3}\frac{dP}{dt} = -\frac{d[Al(BH_4)_3]}{dt} = k_1\,[Al\,(BH_4)_3] + k_c\frac{[Al(BH_4)_3][O_2]_0}{[\text{product}]} \quad (2)$$

From equation (1) it is clear that the rate of aluminum borohydride disappearance is equal to one third of the rate of pressure decline. Furthermore, we can calculate the aluminum borohydride and product pressures

$$P_{Al(BH_4)_3} = P_{0Al(BH_4)_3} - (P_0 - P)/3 \quad (3)$$
$$P_{\text{product}} = (P_0 - P)/3$$

where P, $P_{0Al(BH_4)_3}$ and P_{product} are the total, aluminum borohydride, and product pressures, respectively, at any time; P_0 and $P_{0Al(BH_4)_3}$ are the corresponding initial pressures.

To test equation (2) the rates of reaction at various times were obtained from the slopes of the pressure–time curve. From these values the rates in the absence of oxygen ($3k_1[Al(BH_4)_3]$) were subtracted, and from the resulting quantity and the calculated reactant and product concentrations $k_c[O_2]_0$ was evaluated. The results for a typical run (curve 3 of Fig. 1) are shown in Table I. From the average value of $k_c[O_2]_0 = 2.0 \times 10^{-4}$ we conclude that $k_c = 4.2 \times 10^{-4}$ sec.$^{-1}$ at 49.9°. Several other runs were made, the results of which are summarized in Table II.

TABLE I

CALCULATION OF RATE CONSTANT FROM EXPERIMENTAL DATA

Initial mixture of 52.4 mm. $Al(BH_4)_3$, 51.2 mm. C_2H_4 and 0.48 mm. O_2 at 49.9°; $k_1 = 1.24 \times 10^{-5}$ sec.$^{-1}$)

Time, sec.	dP/dt, mm./sec. $\times 10^3$	Calcd. pressures, mm.		$k_c[O_2]_0$, mm./sec. $\times 10^4$
		$Al(BH_4)_3$	Product	
500	19.3	50.9	1.5	1.7
750	12.8	49.6	2.8	2.1
1000	10.1	48.7	3.7	2.1
1250	9.0	47.9	4.5	2.3
1500	8.3	47.1	5.3	2.5
1750	7.4	46.5	5.9	2.4
2000	6.6	45.9	6.5	2.3
2250	6.1	45.4	7.0	2.3
2500	5.6	44.9	7.5	2.2
2750	5.3	44.4	8.0	2.2
3000	4.9	44.0	8.4	2.1
3250	4.7	43.6	8.8	2.1
3500	4.6	43.2	9.2	2.1
3750	4.3	42.9	9.5	2.0
4000	4.1	42.5	9.9	1.9
4250	3.6	42.2	10.2	1.6
4500	3.6	41.9	10.5	1.7
4750	3.5	41.6	10.8	1.7
5000	3.3	41.3	11.1	1.6
5250	3.1	41.0	11.4	1.5
5500	2.9	40.8	11.6	1.3
			Av.	2.0 ± 0.3

Therefore $k_c = 4.2 \times 10^{-4}$ sec.$^{-1}$

In order to check the hypothesis of product inhibition, a run was made with boron triethyl added to the reaction mixture. The pressure–time curve for this experiment is shown in Curve 4 of Fig. 1. The only effect of the boron triethyl was to eliminate the induction period. Next a run

TABLE II

VALUES OF k_c FOR THE REACTION OF ALUMINUM BOROHYDRIDE WITH ETHYLENE IN THE PRESENCE OF TRACES OF OXYGEN

Reactants pressure, mm.					$k_c[O_2]_0$, mm./sec. $\times 10^4$	k_c, sec.$^{-1}$ $\times 10^4$
$Al(BH_4)_3$	C_2H_4	O_2	$B(C_2H_5)_3$	$Al(BH_4)_2C_2H_5$		
Temperature 49.9°						
52.4	51.2	0.48	..	..	2.0 ± 0.3	4.2
38.7	35.5	.33	..	..	1.3 ± 0.1	3.9
61.3	37.6	.35	..	..	1.4 ± 0.1	4.0
66.9	34.4	.15	..	..	0.62 ± 0.10	4.1
49.1	62.4	.31	25.6	..	1.2 ± 0.2	3.9
62.7	64.4	.27	12.3	12.3	1.2 ± 0.3	4.4[b]
56.8	46.8	.24	..	..	0.33 ± 0.04	1.4[a]
Temperature 64.1°						
44.8	26.9	0.27	..	..	4.0 ± 0.1	15
58.4	30.8	.13	..	..	1.9 ± 0.1	15
28.8	55.2	.44	..	..	6.6 ± 1.4	15
28.0	54.8	.44	..	..	6.1 ± 1.0	14
33.0	40.8	.41	..	..	6.1 ± 0.8	15
32.8	28.8	.15	..	..	2.1 ± 0.3	14
32.4	25.6	.13	..	..	1.8 ± 0.3	14
40.7	19.6	.10	..	..	1.3 ± 0.1	13
41.4	36.8	.20	..	..	2.9 ± 0.6	15

[a] Run in packed reaction bulb. [b] Calculated allowing for $Al(BH_4)_2C_2H_5$ initially present: k_1 at 49.9° = 1.24×10^{-5} sec.$^{-1}$, k_1 at 64.1° = 9.59×10^{-5} sec.$^{-1}$; see ref. 3.

was made in the absence of oxygen so that considerable amounts of boron triethyl and $Al(BH_4)_2C_2H_5$ were formed. Then more ethylene and a trace of oxygen were added. The pressure–time curve for this experiment after the addition of oxygen and ethylene (Curve 5 of Fig. 1) showed more curvature than we would anticipate if equation (2) were rigorously followed. Nevertheless, the steep initial portion of the curve was absent, and the average k_c calculated allowing for the $Al(BH_4)_2C_2H_5$ initially present checked with the values obtained from other runs (although $k_c[O_2]_0$ values from point to point were not as constant). Since boron triethyl alone had no effect in this respect we may attribute the inhibition to $Al(BH_4)_2C_2H_5$.

Finally, a run was performed in a packed reaction vessel. This run has been indicated by a superscript [a] in Table II, and it is seen that the accelerating effect of the oxygen has been counteracted.

A rate expression for the reaction similar to equation (2) may be derived as follows: Assume first a dissociation reaction of aluminum borohydride

$$Al(BH_4)_3 \xrightarrow{k_1} Al(BH_4)_2H + BH_3 \qquad (4)$$

Followed by these rapid reactions

$$Al(BH_4)_2H + C_2H_4 \longrightarrow Al(BH_4)_2C_2H_5 \qquad (5)$$

$$BH_3 + 3\ C_2H_4 \longrightarrow B(C_2H_5)_3 \qquad (6)$$

$$B(C_2H_5)_3 + O_2 \longrightarrow B(C_2H_5)_3O_2 \qquad (7)$$

Next we assumed that $B(C_2H_5)_3O_2$ reacts with aluminum borohydride as

$$B(C_2H_5)_3O_2 + Al(BH_4)_3 \xrightarrow{k_2} BH_3O_2 + B(C_2H_5)_3 + Al(BH_4)_2H \qquad (8)$$

Now BH_3O_2 undergoes a rapid reaction with ethylene, regenerating $B(C_2H_5)_3O_2$

$$BH_3O_2 + 3\ C_2H_4 \longrightarrow B(C_2H_5)_3O_2 \qquad (9)$$

Finally, we assume the following equilibrium exists

$$B(C_2H_5)_3O_2 + Al(BH_4)_2C_2H_5 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} B(C_2H_5)_3O_2{:}Al(BH_4)_2C_2H_5 \qquad (10)$$

From equations (4) and (8) the rate of disappearance of aluminum borohydride is seen to be

$$-\frac{d[Al(BH_4)_3]}{dt} = k_1[Al(BH_4)_3] + k_2[Al(BH_4)_3]\ [B(C_2H_5)_3O_2] \qquad (11)$$

From equation (10) we have

$$k_3/k_4[B(C_2H_5)_3O_2]\ [Al(BH_4)_2C_2H_5] = [B(C_2H_5)_3O_2{:}Al(BH_4)_2C_2H_5] \qquad (12)$$

Assuming the oxygen is present in the form of $B(C_2H_5)_3O_2$ or the complex $B(C_2H_5)_3O_2{:}Al(BH_4)_2C_2H_5$ we may write

$$[O_2]_0 = [B(C_2H_5)_3O_2{:}Al(BH_4)_2C_2H_5] + [B(C_2H_5)_3O_2] \qquad (13)$$

combining equations (12) and (13) we find that

$$[B(C_2H_5)_3O_2] = \frac{[O_2]_0}{1 + k_3/k_4[Al(BH_4)_2C_2H_5]} \qquad (14)$$

which on substitution into equation (11) gives

$$-\frac{d[Al(BH_4)_3]}{dt} = k_1[Al(BH_4)_3] + \frac{k_2[Al(BH_4)_3][O_2]_0}{1 + k_3/k_4[Al(BH_4)_2C_2H_5]} \qquad (15)$$

It is obvious that if $k_3/k_4\ Al(BH_4)_2C_2H_5 >> 1$ equations (2) and (15) are identical in form. It would be well to point out that the variation in $k_c[O_2]_0$ as shown in Table I was quite general; values first increase with time and later fall off again. If we assume that $k_3/k_4 \approx 1$ the initial rise in the values levels off. The later fall must be ascribed to some other process whereby $B(C_2H_5)_3O_2$ is destroyed. If the reaction shown in equation (10) occurs on the surface we are able to understand why the reaction is slowed in a packed reaction bulb. This scheme of reactions also explains the induction period. Thus at the start the reaction proceeds slowly *via* equations (4), (5) and (6). However as soon as boron triethyl is formed it reacts with oxygen, and the reaction is accelerated in an autocatalytic fashion until the oxygen is used up. The reaction of equation (7) is known, having first been observed by Frankland[5]; Bamford and Newitt[6] have shown that in the case of boron tripropyl the reaction occurs very rapidly at room temperature.

In studying the kinetics of the reaction of aluminum borohydride with ethylene the oxygen con-

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[5] Frankland, *J. Chem. Soc.*, **15**, 363 (1862).

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

centration must be kept low or explosion may occur. Thus a mixture of 21.1 mm. $Al(BH_4)_3$, 44.0 mm. C_2H_4 and 0.67 mm. O_2 (65.8 mm. total pressure) exploded at 49.9° after an induction period of 120 seconds. The walls of the reaction bulb were coated with a dense light brown deposit similar in appearance to that found after thermal decomposition of aluminum borohydride. The deposit could be washed out with water. After the explosion the pressure had increased to 93.0 mm. These facts suggest that an explosive decomposition of the aluminum borohydride had taken place; the absence of a carbon deposit would indicate that the ethylene remained substantially unaffected.

Finally a few experiments were performed to determine the amount of aluminum borohydride necessary to ignite a stoichiometric ethylene–oxygen mixture ($C_2H_4 + 3O_2$) at 20°. It was found that the limiting amount of borohydride was 0.46 mm. at 100 mm. total pressure. Similar experiments with boron triethyl showed that about 1.5 mm. were required under the same conditions. The explosions with boron triethyl as an initiator occurred immediately, while those in which aluminum borohydride was used had induction periods of from 18 to 800 seconds. In experiments below the limit (as in the case of the induced combustion of butene-1[2]) the sudden formation of a mist up to 50 seconds after the gases were mixed was noted. The mist formation was accompanied by a rapid drop in pressure, and the time lag in its formation appears to correspond to the induction period in the explosive mixtures. As in the case of the reaction between ethylene and aluminum borohydride in the presence of traces of oxygen, we might expect that boron triethyl would eliminate the induction period. As anticipated, a mixture containing 0.28 mm. of boron triethyl and 2.8 mm. of aluminum borohydride exploded immediately, while mixtures containing similar amounts of borohydride but no boron triethyl had induction periods in the vicinity of 500 seconds.

Thus we are able to understand why aluminum borohydride (a substance which will not react with dry oxygen or oxygen–paraffin mixtures at room temperature) can induce the combustion of olefins.[2] The reaction of aluminum borohydride with olefins[3] leads to the formation of boron alkyls; furthermore this reaction is greatly accelerated in the presence of oxygen. Boron alkyls have been shown to initiate the reaction chain leading to explosion.[6,7] The fact that boron triethyl eliminates the induction period of both explosive and non-explosive reactions in the presence of oxygen confirms our suspicion that boron alkyls play a vital role in the combustion mechanism.

Summary

1. The effect of traces of oxygen on the reaction between aluminum borohydride and ethylene has been studied. It is found that the reaction is accelerated by oxygen and inhibited by a reaction product and by increased surface area. A kinetic equation which qualitatively describes the experimental results is given, and a possible reaction mechanism is proposed.

2. A few experiments on the induced combustion of ethylene with aluminum borohydride and with boron triethyl have been performed. Traces of boron triethyl eliminate the induction period for aluminum borohydride–ethylene–oxygen explosions.

[7] Brokaw, Badin and Pease, THIS JOURNAL, **70**, 1921 (1948).

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[CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Path of Carbon in Photosynthesis. IX. Photosynthesis, Photoreduction and the Hydrogen–Oxygen–Carbon Dioxide Dark Reaction[1]

BY ELMER J. BADIN[2] AND MELVIN CALVIN

It has been shown that certain algae after being allowed to remain in an atmosphere of molecular hydrogen in the dark acquire the ability to reduce carbon dioxide by two processes in addition to the normal reaction of photosynthesis represented by

$$H_2O + CO_2 \xrightarrow{h\nu} (CH_2O) + O_2 \qquad (1)$$

These two additional reactions were first observed by Gaffron[3,4] and are (a) photoreduction (a light induced reaction occurring at low light intensity). No oxygen is

$$2H_2 + CO_2 \xrightarrow{h\nu} (CH_2O) + H_2O \qquad (2)$$

evolved in this reaction. (b) The hydrogen–oxygen–carbon dioxide reaction (a dark reaction).

$$2H_2 + O_2 + xCO_2 \longrightarrow \text{products} \qquad (3)$$

This latter process is presumed to occur as a result of, or be initiated by, the hydrogen–oxygen reaction

$$2H_2 + O_2 \longrightarrow 2H_2O \qquad (4)$$

The ratio of the amount of carbon dioxide reacting to the amount of oxygen present in reaction (3) has not been determined with certainty.

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[1] The work described in this paper was sponsored by the Atomic Energy Commission.

[2] While on leave from the Department of Chemistry, Princeton University, Princeton, New Jersey.

[3] H. Gaffron, *Nature*, **143**, 204 (1939).

[4] H. Gaffron, *Science*, **91**, 529 (1940).