carbon fragments could only result in a complicated mixture of compounds. The observed synthesis of paraffin hydrocarbons from methane and the formation of polymeric solids indicates the complexity of these reactions. It is suggested that in the reaction of diborane with olefins or aromatic hydrocarbons this effect will make isolation of the primary reaction products difficult or impossible if the reaction conditions are severe or if relatively large amounts of diborane are used.

The behavior of the reaction products from benzene and diborane suggests that the intermediate phenyldiboranes, if they are formed, are quite unstable and resemble chlorodiborane rather than the alkyldiboranes. Thus monophenyldiborane may exist at room temperature only in equilibrium with both diborane and triphenylboron. This behavior might be predicted in view of the electronegative character of the phenyl group.

This work has been directed toward outlining the general types of reactions that diborane and hydrocarbons may undergo. It is not unreasonable to assume that under different conditions reaction products other than those observed by the author may be obtained. For example, at lower reaction temperatures it may be possible to isolate intermediate alkylation products of diborane.

Summary

The reactions of diborane with hydrocarbons have been investigated at elevated temperatures using low concentrations of diborane. Under these conditions:

1. The addition of diborane to olefins results in the formation of trialkylborons.
2. A substitution reaction occurs with benzene to form phenylboron compounds.
3. The reactions of diborane with paraffins are complex and involve paraffin chain breakdown and paraffin chain synthesis as well as the formation of boron–carbon bonds.

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[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Spontaneous Ignition of Nickel Carbonyl Vapor. The Ignition of *n*-Butane[1]

BY ELMER J. BADIN, PAUL C. HUNTER AND ROBERT N. PEASE

Earlier papers[2] from this Laboratory have described the spontaneous ignition of zinc dimethyl and of boron triethyl vapors in oxygen, and the oxidation of *n*-butane induced thereby. Similar experiments with nickel tetracarbonyl are here reported.

The apparatus for these experiments was of conventional design.[2] It need only be mentioned that a clean, dry reaction bulb (6.5 cm. diameter) was used for each experiment, and that the bulb was thermostatted at 20°. Nickel carbonyl was obtained through the Matheson Company and fractionated in a nitrogen atmosphere before use (b. p. 43.5°). Oxygen and air were dried before using.

Precise measurements of explosion limits were prevented by the occurrence of long and variable induction periods (up to at least 1000 sec.). Thus, out of 6 experiments on 30 mole % nickel carbonyl in oxygen at 110 to 120 mm. total pressure, explosion occurred almost immediately on admitting the oxygen in two cases; after 30 and 325 seconds in two cases; while there was no explosion in 1000 seconds for two other trials. In another set of 12 experiments on 10% nickel carbonyl in dry air between 150 and 200 mm. total pressure, successes and failures (over 1000 seconds) were spread rather uniformly over the whole pressure range.

The reason for this irreproducible behavior is not clear. In some experiments with long induction periods, a film would form slowly at some point on the surface of the bulb. This could indicate dissociation of the carbonyl, since Mittasch's equilibrium data[3] indicate considerable dissociation at equilibrium even at 20° and 180 mm. A free nickel surface would seem to be ideal as a point from which inflammation could spread. Nevertheless, the formation of a white fog in the body of the gas always immediately preceded explosion, as if the initiating reaction were homogeneous. In this connection it is of interest that Berthelot[4] reported explosions of dry nickel carbonyl–oxygen mixtures at room temperature only if the mixture were abruptly expanded in a buret over mercury, or if the buret were shaken violently. This might suggest ionization due to friction between the mercury and the glass container. Though our mixtures were quiescent at the time of explosion, it is conceivable that an extraneous disturbance is involved. The behavior, however, might be still due to indeterminate differences or non-uniformity in the clean Pyrex surfaces used.

In Table I are reported the lowest pressures at which explosion was observed within 1000 seconds. Minimum values were quite low and only moderately different for oxygen as compared to air,

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[2] E. J. Badin, D. R. Walters and R. N. Pease, THIS JOURNAL, **69**, 2586 (1947); R. S. Brokaw, E. J. Badin and R. N. Pease, *ibid.*, **70**, 1921 (1948).

[3] Mittasch, *Z. physik. Chem.*, **40**, 1 (1902).

[4] Berthelot, *Ann. chim. phys.*, [6] **26**, 555 (1892).

except for mixtures with excess of carbonyl (40%). They are substantially below those reported by Garratt and Thompson[5] and by Bawn[6] at higher temperatures (40–60° 100–45 mm. nickel carbonyl) when oxygen was admitted slowly to the nickel carbonyl vapor. According to these authors, the induction period is still considerable even at the higher temperatures.

TABLE I

LOWEST OBSERVED EXPLOSION PRESSURES OF $Ni(CO)_4$ IN OXYGEN OR AIR AT 20°

Clean Pyrex bulb, 6.5 cm. diameter. Induction periods up to 1000 seconds

$Ni(CO)_4$, mole %	Total press., mm.	Part. press., $Ni(CO)_4$
In oxygen (Stoich. 28.5 mole % $Ni(CO)_4$)		
10	115	12
30	115	35
40	150	60
In air (Stoich. 7.8 mole % $Ni(CO)_4$)		
10	145	15
20	160	32
40	280	112

A summary of analytical data may be added. After explosion, the gas was found to be mainly carbon dioxide (CO_2/CO = 4 to 40). Solid residues varied in composition from 60 to 81.7% Ni (NiO, 79.7% Ni).

Although we are not in a position to suggest a detailed mechanism for nickel carbonyl oxidation, it is tempting to correlate the induction period with a preliminary dissociation of the carbonyl[5]

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO$$

followed by addition of oxygen

$$Ni(CO)_3 + O_2 \longrightarrow Ni(CO)_3 \cdot O_2$$

This would be in contrast to the behavior of the metal alkyls[2] whose unsaturated nature seems to permit direct addition of oxygen with negligible induction periods.

It was also found that nickel carbonyl would cause the explosion of n-butane–oxygen mixtures at 20°. There were long induction periods, and occasional violent explosions. For example, a mixture of 36 mm. of nickel carbonyl, 24 mm. of n-butane, and 140 mm. of oxygen exploded after 550 seconds, shattering the reaction bulb. With somewhat less nickel carbonyl it was possible to preserve the exploded mixtures for analysis, but the temperature had to be raised to 40° in order to obtain explosion in a reasonable time. Analytical data for carbon dioxide, hydrogen and oxygen are reported in Table II, as partial pressures. Olefins and paraffins were found to be present only in negligible amounts. Deficits in the material balance represent nickel compounds, water and other condensable products. The large amounts of carbon monoxide and hydrogen formed from rich mixtures are of interest, and leave no question that the hydrocarbon reacted.

TABLE II

PRODUCTS FROM THE EXPLOSION OF n-BUTANE–OXYGEN MIXTURES INDUCED BY NICKEL CARBONYL

Clean Pyrex bulb, 6.5 cm. diameter. Explosion at 40°, pressures measured at 20°. Initial pressure 200 mm.

Partial pressures, mm.							Final[a] press., mm.
Initial			Final				
$Ni(CO)_4$	n-C_4H_{10}	O_2	CO_2	CO	H_2	O_2	
25	0	175	86	2	0	122	210
25	10	165	131	2	2	41	176
25	18	157	147	17	9	9	182
25	25	150	103	81	45	10	239
25	35	140	62	158	102	7	329
25	45	130	26	223	173	9	431

[a] Corrected for vapor pressure of water, except in first experiment.

Summary

1. Nickel carbonyl vapor explodes in air or oxygen at 20° and partial pressures as low as 15 mm. Explosion is preceded by a long and variable induction period.

2. The existence of an explosion limit and induction period suggests a chain process. The exact mechanism of initiation is not known.

3. Addition of nickel carbonyl to a n-butane–oxygen mixture causes the latter to react at 20–40°.

PRINCETON, NEW JERSEY RECEIVED OCTOBER 18, 1947

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[5] A. P. Garratt and H. W. Thompson, *J. Chem. Soc.*, 1822 (1935).

[6] C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 440 (1935).