aqueous system.[35] Potassium rather than sodium hydroxide was used, and 0.5 *M* lithium chloride was the supporting electrolyte. A very small quantity of a precipitate of undetermined composition appeared on mixing these buffer components; it was allowed to settle and the supernatant liquid had a *p*H, with the glass electrode, of 7.4. This *p*H did not change perceptibly on dilution of the buffer with the alkaline reaction samples. The buffer capacity was relatively high, the acidic form having a concentration about 100 times that of the RDX; this was probably adequate to buffer the electrode reactions.[36]

Analytical Procedure.—Ten-ml. aliquot portions of the reaction solutions were diluted to 100 ml. with buffer and the samples analyzed in triplicate. To each test solution was added four drops of 0.05% methanolic acid fuchsin. The calculated RDX concentration was corrected to the original temperature of the reaction by means of the known temperature dependence of methanol density.[37]

General Techniques in Rate Runs.—For the very slow runs the reaction solutions were sealed in glass ampoules initially, allowed to come to temperature in the thermostated bath, and the concentrations and time obtained at the first titration used as the initial point in the calculation of rate constants. For the more rapid cases the appropriate quantity of base solution was sealed in an ampoule, this ampoule and a volumetric flask containing the RDX solution were allowed to come to temperature, and at zero time the ampoule was broken and the two solutions mixed and shaken vigorously. The nature of the reaction was such that it was very rapid initially and then slow as (largely) k_2 governed the kinetics. Hence after the rate had slowed appreciably the reaction solutions were transferred rapidly to ampoules in order that evaporation losses be minimized. This operation gave no "breaks" in the smoothness of the concentration–time curves, and no correction in time appeared necessary.

Times of reaction were taken when a constant fraction (approximately half) of the aliquot sample had been added to the acid solution (or, in the case of phenolphthalein alkalimetry, to cold water) which arrested the reaction.

The microburets and automatic pipets which were used were calibrated with the appropriate solvents.

Acknowledgments.—It is a pleasure to acknowledge the very excellent work of Richard G. Thrap on the kinetic experiments and calculations. Maynard E. Smith was exceedingly generous with his advice and equipment concerning the polarographic work. The resistance thermometer was kindly loaned by A. Popolato. The writer also wishes to thank his associates, particularly Leon Goodman and Professor Marvin Carmack, for many helpful suggestions and discussions.

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[35] N. A. Lange, "Handbook of Chemistry," Sixth Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1103.

[36] Reference 33, page 112.

[37] "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 27.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A Kinetic Study of the Diborane–Ethylene Reaction[1]

BY ALFRED T. WHATLEY AND ROBERT N. PEASE

RECEIVED AUGUST 10, 1953

The combination of ethylene with diborane yielding boron triethyl as a final product proceeds in the range 120–175° at a rate given by $-dp/dt = k[B_2H_6]^{3/2}/(1 - a[B_2H_6]/[C_2H_4])$. As the equation indicates, the reaction becomes mildly explosive when the B_2H_6/C_2H_4 ratio is sufficiently increased (beyond about 0.5); and the excess of diborane is consumed in the process. A mechanism of ethylene addition is proposed.

Hurd[2] has reported that diborane reacts slowly with excess of ethylene at 100° to yield mainly boron triethyl. Since the process inevitably involves breakage of the boron–boron bond at some stage, it was of interest to determine whether the kinetics would reveal a fractional order in diborane such as has been observed in the decomposition of diborane[3] and in other reactions.

Our curiosity about the diborane–ethylene reaction was further heightened by some observations made in the course of experiments on diborane–oxygen explosions.[4] Such explosions occur after an induction period at 100° and above, within a range of diborane–oxygen compositions. Since it had been shown that low concentrations of boron triethyl react explosively with oxygen at 0°,[5] it had been presumed that addition of ethylene to diborane–oxygen mixtures would enhance the explosibility of the latter *via* initial formation of boron triethyl. However, this did not prove to be the case. On the contrary, ethylene acted as an inhibitor. A partial explanation came from the observation that when an ethylene–diborane mixture in the ratio 2:1 or less[6] was admitted to the hot reaction flask, the pressure first fell and then rose abruptly due apparently to decomposition of a portion of the excess diborane with liberation of hydrogen. Thus, whatever the full explanation of the inhibiting effect of ethylene on the diborane–oxygen explosions might be, it was clear that the reaction of diborane with ethylene alone merited study.

Experimental

Diborane was prepared in the laboratory, and purified by freezing with liquid nitrogen and pumping off any hydrogen present, followed by distillation of the diborane from a melting *n*-butane bath (−135°). At this temperature none of the other boranes has an appreciable vapor pressure. Analysis by hydrolysis indicated less than 2% impurities. The ethylene used was obtained from the Matheson Com-

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[1] Taken from a thesis submitted by Alfred T. Whatley in partial fulfillment of the requirements for the Ph.D. degree. The work described in this paper was jointly supported by Contract NOrd-7920 with the U. S. Naval Bureau of Ordnance as coördinated by the Applied Physics Laboratory, The Johns Hopkins University; and by Contract N6-ori-105 with the Office of Naval Research and Office of Air Research as coördinated by Project Squid, Princeton University. Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted. We wish to acknowledge the assistance of Dean Hugh S. Taylor, who has general supervision of this project.

[2] D. T. Hurd, THIS JOURNAL, **70**, 2053 (1948).

[3] J. K. Bragg, L. V. McCarty and F. J. Norton, *ibid.*, **73**, 2134 (1951); R. P. Clarke and R. N. Pease, *ibid.*, **73**, 2132 (1951).

[4] To be reported. See F. P. Price, *ibid.*, **72**, 5361 (1950).

[5] R. S. Brokaw, E. J. Badin and R. N. Pease, *ibid.*, **70**, 1921 (1948).

[6] The stoichiometric mixture for boron triethyl as product is 6:1.

pany, and the boron triethyl from Dr. R. S. Brokaw of this Laboratory.

In the apparatus used for the kinetic studies, reactions were carried out in a spherical Pyrex reaction flask of 6.6 cm. inside diameter. For the studies on the surface effect, a similar bulb packed with short pieces of Pyrex rod and having a surface-volume ratio about 10 times that of the unpacked flasks was used. While clean flasks were employed from time to time, this did not affect the rate of the reaction materially. The temperature of the reaction bulb was held constant to ±0.1° by a thermostat using silicone oil as the bath liquid. A cut-off manometer was used to connect the reaction flask to the vacuum system, this manometer serving both as a cut-off to ensure constant volume during the reaction and as a means of following pressure changes. A storage flask for the ethylene was attached to the system, as was a bulb containing the diborane. The latter was connected to the system through a mercury cut-off to prevent possible contamination by stopcock grease. An ampoule of boron triethyl was attached to the apparatus in a similar manner.

Calculated quantities of diborane and olefin were premixed at room temperature in a flask of known volume. The mixture was then admitted to the reaction bulb, which was at the desired temperature, and the clock started. The mercury in the cut-off was raised, a vacuum applied to the external system, and the change of pressure with time was followed. Preliminary runs indicated that the amount of reaction between diborane and ethylene at room temperature was slight, if it occurred at all.

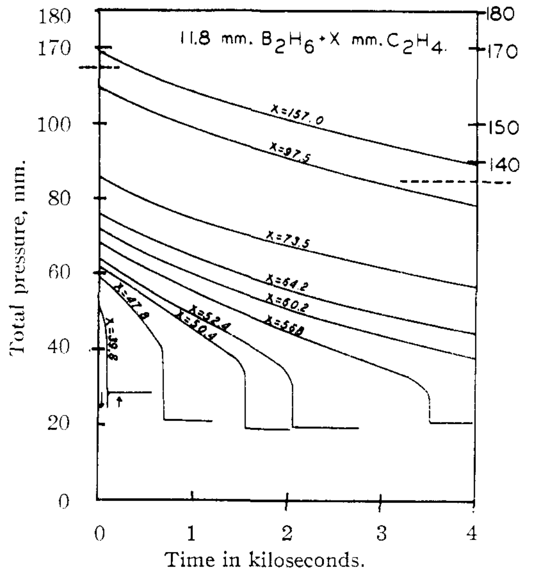

Fig. 1.—Pressure-time curves for ethylene-diborane mixtures at 154°.

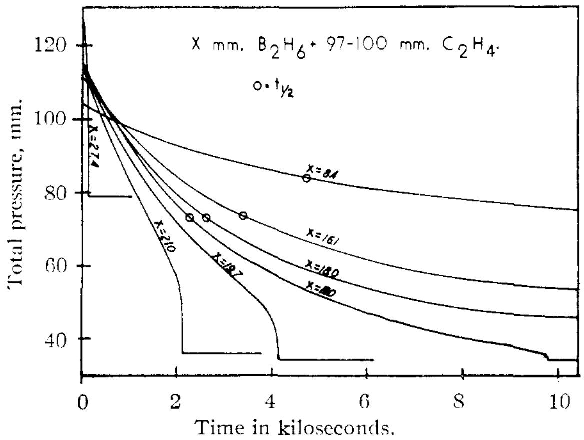

Fig. 2.—Pressure-time curves for ethylene-diborane mixtures at 154°.

Results and Discussion

Typical pressure-time plots are shown in Figs. 1 and 2. In Fig. 1 the curves refer to mixtures containing initially about 12 mm. of diborane and varying amounts of ethylene at 154°. It will be noted that the slopes only change slowly with the initial ethylene concentration so long as the latter remains above or near stoichiometric ratio for boron triethyl formation (1 B_2H_6:6 C_2H_4). Even for somewhat lower initial ratios the initial rate is not much affected; but as reaction proceeds and the ratio falls still further under these conditions, an acceleration sets in. Finally—and this is only just observable in the lowest curve—the pressure drop is replaced by a sharp rise corresponding to decomposition of a portion of the residual diborane. The effect is actually a little greater than the curve would indicate. If the ethylene had all gone to boron triethyl and the residual diborane had remained unchanged, the final pressure would have been 18.2 mm. The observed value (28.8 mm.) corresponds roughly to decomposition of the remaining diborane to boron and hydrogen. In the remaining cases shown in the graphs, the final pressure was always close to that expected for boron triethyl formation.[7]

Similar runs in which the initial ethylene pressure was constant at 97–100 mm. and the diborane was varied are shown in Fig. 2. It is evident that there is a substantial effect of diborane concentration. Comparison of half-lives (shown by circles on the upper four curves) reveals a gross reaction order between one and two.[8]

Further investigation indicated that there was an appreciable effect of surface on the rate. Thus, when the reaction vessel was packed with Pyrex tubing, the rate increased by a factor of 2 to 3. This was for a surface-volume ratio of 10–12 cm.$^{-1}$ as compared to 0.9 cm.$^{-1}$ for the unpacked reaction vessel.

It was also shown that initial addition of boron triethyl (the product) in amounts approximating the initial diborane concentration likewise increased the rate by a factor of about 2, so that the reaction is to some extent autocatalytic. The reason for this is presumably to be sought in a series of reversible exchange reactions known to occur between diborane and boron triethyl whereby substituted diboranes are formed.[9] These reactions may well contribute to the rate of fixation of ethylene, but they can hardly be essential to the initiation of reaction since no induction periods were observed.

For purposes of further analysis, initial rates of pressure drop are compared with initial concentrations in Table I. As already mentioned, there is a pronounced increase in rate as the diborane concentration is increased (ethylene roughly constant).

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(7) Boron triethyl was independently identified in one case by condensing out a sample and running it against a known sample in the mass spectrograph.

(8) A few experiments with propylene and with butene-1 indicated similar behavior with rates about twice those for ethylene.

(9) H. I. Schlesinger, L. Horvitz and A. B. Burg, THIS JOURNAL, **58**, 407 (1936). Also **57**, 621 (1935), **61**, 1078 (1939), for corresponding processes among methylboranes.

This effect could be accommodated roughly by the equation

$$-[\mathrm{d}p/\mathrm{d}t]_0 = k_{3/2}[\mathrm{B_2H_6}]^{3/2}$$

when the B_2H_6:C_2H_4 ratio was not too far from stoichiometric for boron triethyl formation (1 B_2H_6:6 C_2H_4). Values of $k_{3/2}$ are given in the next-to-last column of Table I.

TABLE I

INITIAL RATES OF THE DIBORANE–ETHYLENE REACTION

Init. press., mm. B_2H_6	Init. press., mm. C_2H_4	Init. rate, mm./sec.	$k_{3/2}$, mm.$^{-1/2}$ sec.$^{-1}$	k_{exp} mm.$^{-1/2}$ sec.$^{-1}$
Temp. 130.0°				
8.5	102.9	0.47×10^{-3}	1.9×10^{-5}	1.6×10^{-5}
14.2	88.3	1.30	2.4	1.6
23.3	94.1	3.85	3.4	1.7
23.1	143.5	2.70	2.4	1.7
23.8	197.0	2.82	2.4	1.8
Temp. 143.4°				
7.4	98.6	0.18×10^{-2}	0.9×10^{-4}	7.6×10^{-5}
11.5	98.5	.38	1.0	7.5
17.2	97.8	.79	1.1	7.2
20.8	97.1	1.25	1.3	7.5
25.2	97.8	2.05	1.6	7.9
Temp. 154.5°				
8.4	96.4	0.70×10^{-2}	2.9×10^{-4}	2.4×10^{-4}
10.6	97.9	1.01	2.9	2.3
16.1	98.0	2.23	3.5	2.3
21.0	96.3	3.92	4.1	2.3
24.2	98.4	6.45	5.4	2.3
11.9	45.7	2.17	5.3	2.5
11.7	50.4	1.70	4.3	2.3
11.8	60.2	1.46	3.6	2.2
11.8	73.5	1.34	3.3	2.2
11.8	97.5	1.25	3.1	2.4
11.9	157.0	1.00	2.4	2.1
8.4	50.0	0.70	2.9	2.1
8.4	96.4	.70	2.9	2.4
8.5	194.0	.77	3.1	2.8
8.1	245.0	.87	3.8	3.5
8.3	470.5	.96	4.0	3.9
Temp. 163.2°				
7.8	98.1	1.34×10^{-2}	6.2×10^{-4}	5.2×10^{-4}
11.8	84.5	2.86	7.2	5.1
20.7	99.6	7.84	8.3	4.9
11.9	55.1	3.94	9.6	5.5
11.7	65.0	3.06	7.7	4.9
11.8	84.5	2.86	7.2	5.1
11.8	165.9	2.63	6.5	5.6
11.8	199.4	2.63	6.5	5.7
Temp. 177.2°				
5.2	98.6	0.29×10^{-1}	2.4×10^{-3}	2.2×10^{-3}
11.7	99.0	1.13	2.8	2.2
15.4	92.5	1.82	3.0	2.0
20.4	96.0	3.59	3.9	2.2
11.9	53.7	2.21	5.4	3.0
11.9	57.7	1.83	4.5	2.6
11.9	66.0	1.34	3.3	2.1
11.7	81.8	0.94	2.4	1.7
11.6	120.2	0.90	2.3	1.8
11.8	213.9	0.99	2.4	2.2

The effect of varying initial ethylene concentration (diborane constant) is somewhat less conventional. In the neighborhood of the stoichiometric ratio the rate changes only slowly, but on the whole *increases* as the ethylene concentration *decreases;* though in one series at 154.5° with very large excess of ethylene there was an apparent reversal, the rate increasing slowly as the ethylene concentration was increased. Ignoring the latter for the moment, it was found that the effect of ethylene could be expressed as a correction term involving the B_2H_6/C_2H_4 ratio. The corrected equation then became

$$-[\mathrm{d}p/\mathrm{d}t]_0 = k_{\mathrm{exp}}\frac{[\mathrm{B_2H_6}]^{3/2}}{1 - a\dfrac{[\mathrm{B_2H_6}]}{[\mathrm{C_2H_4}]}}$$

The value of the constant, a, was taken as 2.0 throughout, though there was some suggestion of an increase with temperature. Values of the constant, k_{exp}, are given in the last column of Table I. The effect of temperature on k_{exp} may be expressed by the equation

$$k_{\mathrm{exp}} = 1.5 \times 10^{15}\, e^{-36800/RT}\ \mathrm{mm.}^{-1/2}\ \mathrm{sec.}^{-1}$$

A mechanism to account for these data has been arrived at as follows. The equilibrium reaction

$$\mathrm{B_2H_6} \rightleftarrows 2\mathrm{BH_3}\colon [\mathrm{BH_3}] = K_1{}^{1/2}[\mathrm{B_2H_6}]^{1/2} \qquad (1)$$

is assumed to control the BH_3 concentration. The dependence of rate on the 3/2 power of [B_2H_6] is ascribed to what may be loosely defined as a catalysis of the ethylene addition reaction by the BH_3 radical in the sequence[10]

$$\mathrm{B_2H_6} + \mathrm{BH_3} \longrightarrow \mathrm{B_3H_9} \qquad (2)$$

$$\mathrm{B_3H_9} + \mathrm{C_2H_4} \longrightarrow \mathrm{B_2H_5Et} + \mathrm{BH_3} \qquad (3)$$

The substituted diborane then reacts in the same sense

$$\mathrm{B_2H_5Et} + \mathrm{BH_3} \longrightarrow \mathrm{B_3H_8Et} \qquad (4)$$

$$\mathrm{B_3H_8Et} + \mathrm{C_2H_4} \longrightarrow \mathrm{B_2H_4Et_2} + \mathrm{BH_3} \qquad (5)$$

To take account of the term involving the B_2H_6/C_2H_6 ratio, it is further assumed that the substituted diboranes (after the first) can also react with diborane itself

$$\mathrm{B_2H_4Et_2} + \mathrm{BH_3} \longrightarrow \mathrm{B_3H_7Et_2} \qquad (6)$$

$$\mathrm{B_3H_7Et_2} + \mathrm{B_2H_6} \longrightarrow 2\mathrm{B_2H_5Et} + \mathrm{BH_3} \qquad (7)$$

reaction 7 being in competition with

$$\mathrm{B_3H_7Et_2} + \mathrm{C_2H_4} \longrightarrow \mathrm{B_2H_3Et_3} + \mathrm{BH_3} \qquad (8)$$

Since two molecules of substituted diborane are formed from one in reaction 7, the rate of ethylene fixation is ultimately increased. Logically, such a step should be included at each stage of the substitution, but for simplicity only one such is assumed. Further reactions resembling 6 and 8, or 4 and 5, then lead ultimately to boron triethyl

$$\mathrm{B_2H_3Et_3} + \mathrm{BH_3} \longrightarrow \mathrm{B_3H_6Et_3} \qquad (9)$$

$$\mathrm{B_3H_6Et_3} + \mathrm{C_2H_4} \longrightarrow \mathrm{B_2H_2Et_4} + \mathrm{BH_3} \qquad (10)$$

$$\mathrm{B_2H_2Et_4} + \mathrm{BH_3} \longrightarrow \mathrm{B_3H_5Et_4} \qquad (11)$$

$$\mathrm{B_3H_5Et_4} + \mathrm{C_2H_4} \longrightarrow \mathrm{B_2HEt_5} + \mathrm{BH_3} \qquad (12)$$

$$\mathrm{B_2HEt_5} + \mathrm{BH_3} \longrightarrow \mathrm{B_3H_4Et_5} \qquad (13)$$

$$\mathrm{B_3H_4Et_5} + \mathrm{C_2H_4} \longrightarrow 2\mathrm{BEt_3} + \mathrm{BH_3} \qquad (14)$$

The over-all rate is then given by

$$\begin{aligned}\mathrm{d}[\mathrm{BEt_3}]/\mathrm{d}t &= 2k_{14}[\mathrm{B_3H_4Et_5}][\mathrm{C_2H_4}] \\ &= 2k_8[\mathrm{B_3H_7Et_2}][\mathrm{C_2H_4}] \\ &= \frac{2k_2K_1{}^{1/2}[\mathrm{B_2H_6}]^{3/2}}{1 - (k_7[\mathrm{B_2H_6}]/k_8[\mathrm{C_2H_4}])}\end{aligned}$$

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[10] Reaction 1 has already been employed in the diborane pyrolysis complex of reactions.[8]

Comparison with the experimental equation reveals that

$$2k_2K_1^{1/2} = \frac{2}{5}k_{\text{exp}}$$

$$k_7/k_8 = a = 2.0$$

It will be clearly understood that this correlation rests on the questionable assumption that the initial rate of pressure drop corresponds exactly to the over-all reaction

$$B_2H_6 + 6C_2H_4 \longrightarrow 2BEt_3$$

This assumption will obviously be in error to the extent that substituted diboranes accumulate as intermediates. Experimental determination of such accumulation poses a difficult problem owing to the interactions that are known to occur,[9] and has not been attempted. It is possible that the small apparent increase in rate with very large excess of ethylene in the one series at 154.5° may be accounted for in this way.

A final word may be added concerning the mild "explosion" which follows when the B_2H_6/C_2H_4 ratio is sufficiently large. The limit is, of course, to be identified with the denominator in the rate equation. Since the experimental constant, a, is taken as equal to 2.0, explosion should follow when the B_2H_6/C_2H_4 ratio exceeds 0.5. Actually, no good rate measurements could be obtained for initial values of the ratio greater than about 0.3 due to acceleration as reaction proceeded; and in early trials with a ratio of unity, the "explosion" followed immediately. The observed pressure increase under these circumstances is attributed to involvement of the excess of diborane in the process.

PRINCETON, N. J.

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Nickel, Copper and Some of their Alloys as Catalysts for Ethylene Hydrogenation[1]

BY RICHARD J. BEST[2] AND W. WALKER RUSSELL

RECEIVED JULY 23, 1953

The activity of nickel, copper and some of their alloys as catalysts for the hydrogenation of ethylene has been measured. These catalysts were prepared by the reduction of oxides obtained from the precipitated or coprecipitated metal carbonates. X-Ray examination of these catalysts indicates that they have the lattice constants of recorded equilibrium alloys. No simple relation is found between the activity of the catalysts and their metallic composition. A plausible explanation of catalyst activity appears possible in terms of the known electronic structure of the non-ideal nickel–copper system.

Introduction

Nickel, copper and their alloys have been studied by various investigators interested in the catalytic properties of these metals and their solid solutions. Thus Rienäcker and Bommer[3] studied the hydrogenation of ethylene over such catalysts in foil form between 400 and 500° and reported a marked drop in catalytic activity between alloy compositions of 80.2 and 80.8 atom % of copper, in which composition region the catalyst color changed from light grey to reddish. Using nickel, copper and mixed metal catalysts for the hydrogenation of benzene, Long, Frazer and Ott[4] on the basis of simultaneous X-ray diffraction studies showed that the reduction of the coprecipitated oxides produced active catalysts composed of the same substitutional type of solid solution obtained by melting the component metals together. Reynolds[5] studied the activities of a series of reduced carbonates of nickel and/or copper precipitated on kieselguhr for the hydrogenation of styrene, and also made magnetic susceptibility measurements upon these supported catalysts. In the present work the activity of reduced unsupported precipitated or coprecipitated carbonates of nickel and/or copper for the hydrogenation of ethylene has been studied. Also the surface areas and the lattice constants of the catalysts have been determined. The results appear to find adequate explanation in terms of the known electronic structure of the nickel–copper system.

Experimental

Apparatus and Purification of Gases.—Electrolytic hydrogen, and C.P. ethylene were metered and purified as already described.[6] The helium and likewise the nitrogen used in the adsorption measurements were purified essentially as earlier described.[6]

The catalyst chamber, which was placed in a bath of temperature-regulating liquid, consisted of a vertical Pyrex tube of 15 mm. o.d. in which was axially sealed a 5 mm. o.d. thermocouple well which extended about two-thirds of the way to the bottom of the catalyst bed. Catalyst exit gases passed through a three-way stopcock into a trap containing an aqueous acidified sodium sulfate solution[7] and to waste except when collected in an improved form of constant-head gas buret described elsewhere.[6] When the reaction velocity measurements had been completed upon a given catalyst, the catalyst chamber was sealed to a high vacuum adsorption apparatus generally similar to that described earlier.[8] This seal and the one closing the lower end of the catalyst chamber were made in a stream of purified nitrogen so as to protect the catalyst.

Preparation and Reduction of Catalysts.—The catalysts were prepared by dissolving the calculated amounts of analytical reagent grade $Cu(NO_3)_2 \cdot 3H_2O$ and/or $Ni(NO_3)_2 \cdot 6H_2O$ in water then diluting to correspond to about 5 g. of NiO and/or CuO per 100 ml. To this solution, while rapidly stirred at room temperature, powdered reagent

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(1) This paper is based on a portion of a thesis presented by R. J. Best in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1953.

(2) Metcalf Fellow, 1950–1951, and University Fellow, 1951–1952.

(3) G. Rienäcker and E. A. Bommer, *Z. anorg. allgem. Chem.*, **242**, 302 (1939).

(4) J. H. Long, J. C. W. Frazer and E. Ott, THIS JOURNAL, **56**, 1101 (1934).

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(7) K. A. Kobe and F. H. Kenton, *Ind. Eng. Chem., Anal. Ed.*, **10**, 76 (1938).

(8) W. W. Russell and L. G. Ghering, THIS JOURNAL, **55**, 4468 (1933).