

80. *The Metal-catalysed Reaction between Acetylene and Hydrogen. Part III. Some Effects of Added Substances on the Reaction over Nickel.*

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Reaction over nickel on a number of carrier substances (chiefly oxides) differs little from that over nickel-pumice. No influence of carbon dioxide or nitrogen is detected. More than *ca.* 3% of nitric oxide retards reaction and lowers the yield of ethylene slightly; liquids containing nitrogen are formed. Some reduction of nitric oxide by hydrogen probably occurs. Oxygen retards reaction and raises the ethane yield. It is removed partly as water, but also reacts with the catalyst, its effects persisting during several succeeding experiments.

Silica, titania, thoria, zinc oxide, and chromium sesquioxide catalyse polymerisation in acetylene alone at 200° or below.

THE acetylene-hydrogen reaction on nickel has been studied with various catalyst carriers, chiefly kieselguhr (*e.g.*, Yoshikawa, *Bull. Chem. Soc. Japan*, 1932, 7, 201; Pichler, *Ges. Abh. Kennt. Kohle*, 1934, 11, 395; Ackermann, *Brennstoff-Chem.*, 1937, 18, 357); with this carrier, as with unsupported nickel, reaction appears to be little different from that on nickel-pumice (Parts I and II, *J.*, 1944, 373; this vol., p. 133). With more reactive supports, such as zinc chloride or phosphoric acid, a considerable influence of carrier and metal : carrier ratio is reported (Petrov and Antsus, *Bull. Acad. Sci. U.R.S.S., Classe sci. chim.*, 1940, 274). An influence of metal dispersity with a kieselguhr base (Yoshikawa, *loc. cit.*) remains unconfirmed. Little is known of the effects of oxides as carriers, and further study of these is now reported. In supplement to this, the effects of various oxides on acetylene alone have been examined, since the few previous data usually do not provide clear evidence of the influence of such substances at temperatures below *ca.* 350° (see, *e.g.*, Egloff, "The Reactions of Pure Hydrocarbons," 1937, p. 442).

Dilution with, *e.g.*, carbon dioxide, nitrogen, methane, or steam has been claimed to raise the yields of C₂ hydrocarbons from acetylene and hydrogen over cheap catalysts such as nickel (U.S.P. 1,308,777; D.R.-PP. 350,429, 552,008; cf. D.R.-P. 262,541). The effects are unconfirmed unless they consist simply in prevention of overheating of the catalyst (*e.g.*, Dupont and Lombard, *Bull. Soc. chim.*, 1941, 8, 851). Further tests leading to this conclusion, and also the effects of nitric oxide and oxygen, are now reported.

EXPERIMENTAL.

Gases.—For flow experiments, cylinder acetylene was passed through towers containing concentrated sodium bisulphite and aqueous sodium hydroxide. Hydrogen, and the acetylene for other experiments, were as described in Part I. Nitric oxide was prepared by the action of ferrous sulphate solution on a mixture of concentrated sulphuric acid and potassium nitrate. Other gases were obtained from cylinders.

Catalysts.—(For metal : carrier ratios, see note to Table I.) The nickel-pumice catalysts were those described in Part I. The catalyst on commercial activated alumina was made in an analogous manner, the final reduction being by hydrogen and methanol vapour at 350–400° for 3 hrs. Water-glass was added to certain catalysts to make them sufficiently coarse for use in flow experiments; nickel nitrate solution was evaporated in the presence of the appropriate oxide (commercial grade), water-glass solution evaporated in the presence of the product, and the residue heated to 300–350° for several hours. Catalyst 2 (see Table I) was reduced by ethanol vapour in nitrogen at 400° for 2–3 hrs., catalyst 3 by hydrogen containing ethanol vapour at 490° for 2 hrs. Others containing water-glass were reduced by hydrogen containing methanol vapour at 350–400° for 3 hrs. This treatment will reduce vanadium pentoxide to the tri- or tetra-oxide. Catalysts on precipitated alumina were made by two methods: (1) (adapted from Zelinsky and

Kommarevsky, *Ber.*, 1924, **57**, 667) aluminium nitrate was treated with sodium hydroxide till the precipitate was just redissolved, nickel nitrate solution added, and the mixture saturated with carbon dioxide; the precipitate was washed, dried, ignited, and reduced in hydrogen at 300° for 12 hrs.; (2) mixed solutions of nickel and aluminium nitrates were treated at 50–55° with sodium hydroxide, and the dried precipitate (a hard gel) heated to 400° in nitrogen and reduced as in (1).

For tests of their effect on acetylene alone, gels of alumina, silica, titania, chromium sesquioxide, and zinc oxide were prepared as follows (the titania and zinc oxide were kindly supplied by Dr. P. H. Given): (a) treatment of aluminium nitrate (50% soln.) at 50–55° with the equivalent of 6% sodium hydroxide; (b) treatment of commercial sodium silicate (in 20% soln.) at ca. 50° with ca. one-third of its weight of hydrogen chloride as 2.3% solution; (c) dropping titanium tetrachloride into 10% ammonia and boiling the product; (d) treatment of chromic nitrate (6%) at 78–84° with slight excess of 17% ammonia, followed by dilution and boiling; (e) treatment of a cloudy 5.7% solution of zinc chloride (600 c.c.) at 40–63° with 425 c.c. of 5.9% sodium hydroxide, followed by dilution and boiling. The precipitates were washed and dried in air or nitrogen, usually at 300–350°. Specimens (2–4 g.) of these oxides, and also of commercial thoria and acid-washed kieselguhr, were finally heated to 300° under high vacuum in the reaction bulb until their water-vapour pressures were very small.

Apparatus.—For constant volume runs this was the same as in Part I. The flow apparatus was mainly of all-glass type. Gases (from flow-meters) were mixed in a tower over alkaline pyrogallol, and traversed 3–5 g. of catalyst in the central 10 cm. of a 40-cm. electrically heated tube (1 cm. diam.). A coated thermocouple, in the catalyst, recorded the temperature. After passing through a trap at ca. –10° (and sometimes one at –78°), gases were collected at constant pressure (ca. 1 atm.) over saturated salt solution. Flow-meters were calibrated as described by Meuron (*Ind. Eng. Chem. Anal.*, 1941, **13**, 114). Errors due to solubility of acetylene were minimised by driving that gas, during calibration, with saturated salt solution, kept fully saturated with acetylene by suitable precautions, and also by transferring gases awaiting analysis, under slight excess pressure, to bulbs isolated from the salt solution. All flow-rates were converted to terms of dry gas at N.T.P. Exothermic reaction was usually evident over catalysts pre-heated to 350° in hydrogen. After the steadiest possible conditions had been maintained for ca. 1 hr., approximately 1 l. of gas was collected. The rate of collection often increased during a run, on account of a decline in catalyst activity. For a large extent of reaction in these runs, a maximum error of ca. ±3% (of the unrecovered acetylene) in the ethylene yield appears reasonable, with ±1% for the smaller ethane yields.

Gas Analysis.—Carbon dioxide was absorbed before the usual analysis (see Part I). Tests for nitric oxide were made by adding a measured excess of oxygen and exposing the gases to potassium hydroxide.

RESULTS AND DISCUSSION.

(i) *Influence of Catalyst Carrier.*—The results are summarised in Table I, the contact times being ca. 2–6 secs. (in all tables, C_mH_n represents unsaturated hydrocarbons higher than the C_2 series). On kieselguhr-water-glass (catalysts 2 and 3) the yields of C_2 hydrocarbons (as fractions of the unrecovered acetylene) seem slightly higher than on pumice (catalyst 1); ethylene is the chief C_2 product, as with all the carriers tested. On activated alumina (catalyst 4) the lowest ethylene yield is recorded. On precipitated alumina (catalysts 5 and 6) the yields resemble those on catalysts 1–3, as was confirmed for catalyst 6 by experiments at constant volume at 17–105°. On vanadium oxide-water-glass (catalyst 7) the yields resemble those with pumice, but a lower ethylene yield is recorded on chromium sesquioxide-water-glass (catalyst 8).

The group of three runs over catalyst 5 in Table I are successive 1-hr. stages of one experiment; the yields are little affected by decreasing activity of the catalyst.

Catalyst 4 had little effect on acetylene alone in ca. 6 secs. at 170° (Table I); catalyst 5 caused rapid decomposition of acetylene at 316°.

Over all catalysts, products other than C_2 hydrocarbons account for removal of more acetylene than

TABLE I.
Flow experiments over nickel on different carriers.

Catalyst No.*	Temp. (±5°).	Flow rates (l./hr.).			Product (vol. % to nearest unit %).					Yield (%).		
		C_2H_2 .	H_2 .	Gaseous product.	C_2H_2 .	C_mH_n .	C_2H_4 .	H_2 .	C_2H_6 .	% C_2H_2 reacted.	C_2H_4 .	C_2H_6 .
1	178°	1.06	1.00	0.67	10	12	52	16	7	94	35	5
2	177	2.70	2.41	1.89	20	12	53	6	7	86	43	5
	183	2.73	2.47	1.94	20	14	50	5	7	86	41	6
	130	2.84	2.53	2.00	17	13	53	7	8	88	42	6
2	131	2.85	2.56	2.01	18	13	53	6	9	87	43	7
	212	2.39	2.50	1.80	7	13	54	14	11	95	43	9
	214	2.42	2.57	1.82	6	13	54	14	10	95	43	8
3	141	1.12	1.03	0.96	25	8	41	18	7	79	45	7
4	147	1.36	1.25	0.54	9	1	48	15	23	96	20	9
	170	2.23	—	2.13	97	—	1	—	—	—	—	—
5	150	1.32	1.27	0.63	1	1	76	4	16	99	36	8
	150	1.43	1.34	0.74	5	1	72	7	14	97	38	7
5	150	1.43	1.32	0.77	12	1	67	8	11	94	39	6
	150	1.43	1.28	0.93	21	1	56	11	9	86	42	7
6	150	1.17	1.17	0.78	23	1	39	24	10	84	31	8
7	140	1.46	1.47	0.83	3	1	60	25	10	98	35	6
8	138	1.54	1.43	0.70	3	1	54	31	9	99	25	4

* Numbering of catalysts (weight-ratios are given).—1 = 1 nickel : 10 pumice; 2 = 3 nickel : 10 kieselguhr : 10 water-glass; 3 = 2 nickel : 10 kieselguhr : 10 water-glass; 4 = 1 nickel : 5 commercial activated alumina; 5 = 2 nickel : 5.5 precipitated alumina (method 1); 6 = 1 nickel : 8.5 precipitated alumina (method 2); 7 = 2 nickel : 10 water-glass : ca. 10 vanadium oxide; 8 = 2 nickel : 10 chromium sesquioxide : 10 water-glass. Brackets against catalyst numbers embrace experiments made on the same specimen of catalyst.

hydrogen (acetylene : hydrogen ratio in these products = 1.1—1.5). Removal of acetylene in this form can be favoured, *e.g.*, by alumina or chromium sesquioxide; this is probably related to the effects of such oxides themselves on acetylene (see below). The structures of the products other than C_2 hydrocarbons may be influenced by the catalyst carrier, but in the cases listed there is a general resemblance to reaction over nickel-pumice.

Tests were also made of the action of some possible catalyst supports on acetylene alone at 17—384°. Table II summarises a comparison of reaction in acetylene in a Pyrex bulb with that in the presence of various oxides (Δp = pressure-fall measured at constant volume; t = duration in mins.). The last col. records the phenomena observed on withdrawing the gas.

TABLE II.

Catalyst.	Temp.	Initial press. of C_2H_2				% C_2H_2 in product gas.	Fog	Catalyst.	Temp.	Initial press. of C_2H_2				% C_2H_2 in product gas.	Fog
		(mm.).	Δp .	t .						(mm.).	Δp .	t .			
None	445°	520	75	35	97	Fog	ThO_2	{ 98°	392	78	11	98.7	No fog		
Kieselguhr	384	495	27	36	98	Slight fog		{ 180	455	118	11	98.9	No fog		
Al_2O_3	{ 276	425	100	19	96.3	No fog	Cr_2O_3	{ 185	417	145	30	97.4	No fog		
		{ 313	490	440	15	—		{ 230	432	163	6	95.4	No fog		
SiO_2	{ 356	495	208	21	94	Fog	ZnO	{ 257	492	102	16	98	Fog		
		{ 308	450	115	25	97		No fog	{ 316	502	215	28	94	Fog	
TiO_2	{ 115	406	130	30	99	No fog									
		{ 267	474	210	7	97	Slight fog								

Without a catalyst, reaction was very slow below 350—400°, and at 445° was mainly polymerisation; hydrogen, if added, acted chiefly as a diluent. Kieselguhr produced at the most a slight acceleration, but all the other substances induced reaction (predominantly polymerisation, with production of only traces of other gases) under conditions which leave acetylene unchanged for long periods. The active substances all adsorbed *ca.* 2—6 c.c. of acetylene (at N.T.P.) per g. at *ca.* 400 mm. and 20°. As the temperature was raised, adsorption decreased, and was eventually followed by a slower continued fall in pressure due to polymerisation, which was readily detected at *ca.* 100° for titania, thoria, and chromium sesquioxide and *ca.* 200° for alumina, silica, and zinc oxide. The oxides became discoloured by adsorbed hydrocarbons and, in time, less active in polymerising acetylene. No free carbon was found, except possibly with titania, which became black throughout the granules, though polymerisation was still the main reaction.

The results with alumina confirm those of Boswell and Dilworth (*J. Physical Chem.*, 1925, 29, 1489). Stannous oxide has a similar effect (Pearce and Goergen, *ibid.*, 1928, 32, 1423). Berl and Hofmann (*Z. angew. Chem.*, 1931, 44, 259) reported that silica (and also stannic and calcium oxides) favoured decomposition rather than polymerisation; decomposition and polymerisation were reported over zinc oxide on charcoal at 370°. The somewhat different results of the present research (cf. also B.P. 334,203) may be in part due to differences in conditions. The effects of titania, thoria, and chromium sesquioxide have not been previously investigated.

The suggestion (Morris and Reyerson, *J. Physical Chem.*, 1927, 31, 1332) that ethylene production from acetylene and hydrogen is favoured by a carrier substance (*e.g.*, silica) which adsorbs acetylene more strongly than hydrogen is probably unjustified, since it is based on the view that strongly adsorbed hydrogen and weakly adsorbed acetylene react on the metal, whereas the reverse is true on all metals on which the reaction kinetics are known. Even at the surface of palladium, acetylene is the more strongly adsorbed reactant (Fischer and Knorr, *Z. Elektrochem.*, 1937, 43, 608; Cremer, Knorr, and Plieninger, *ibid.*, 1941, 47, 737), and it seems unlikely that any added substance will greatly favour hydrogen adsorption relative to acetylene adsorption, though this might decrease the yield of reduced polymers of acetylene. Conversely, substances which induce polymerisation of acetylene, or even adsorb that gas strongly, are probably to be avoided as catalyst carriers if high yields of C_2 hydrocarbons are desired, though their effect may not be large in the time of reaction (cf. Table I).

(ii) *Effects of Carbon Dioxide and Nitrogen.*—It was shown by experiments at constant volume that large proportions of carbon dioxide had scarcely any influence on the rate or products of the acetylene-hydrogen reaction at 79° over nickel-pumice. Nitrogen also behaved as an inert diluent in flow experiments.

(iii) *Effect of Nitric Oxide.*—Table III summarises results over nickel-kieselguhr-water-glass catalysts under conditions similar to those of the runs in Table I, but with nitric oxide added (the nitric oxide contents are given as volume percentages of the mixed gas before reaction).

More than *ca.* 1—2% of nitric oxide in the mixture caused some suppression of reaction. The yields of ethylene were depressed slightly by 3.6—6.5% of nitric oxide, but those of ethane were little affected (cf. Table I). The gaseous products contained no appreciable nitric oxide. The liquid products contained nitrogen, were darker than those obtained in the absence of nitric oxide, and had a most unpleasant odour. Ammonia and water were also formed.

These facts suggest that the nitric oxide is reduced by hydrogen, ultimately to ammonia (Neogi and Adhichary, *Z. anorg. Chem.*, 1910, 69, 209; Guye and Schneider, *Helv. Chim. Acta*, 1918, 1, 33). No reaction between acetylene and nitric oxide was detected in short contact times over the same catalysts at *ca.* 200°. In the presence of hydrogen, some nitric oxide may have been removed in terminating radical polymerisation chains on the catalyst (cf. Part II; such termination can apparently occur in gaseous acetylene polymerisation—see,

304 *The Metal-catalysed Reaction between Acetylene and Hydrogen. Part III.*

e.g., Burnham and Pease, *J. Amer. Chem. Soc.*, 1942, **64**, 1404), but the failure of nitric oxide to raise the yield of C₂ hydrocarbons does not support this. The capacity of nitric oxide for destroying free radicals may well be removed if that gas is chemisorbed. Nitrogen may enter the organic products at some stage during the

TABLE III.

Effect of nitric oxide on flow experiments over nickel-kieselguhr-water-glass catalysts.

Catalyst No.*	Temp. (±5°)	Flow rates (l./hr.)		NO, %	Gaseous product rate (l./hr.)	Product (vol. % to nearest unit %)					% C ₂ H ₂ reacted.	Yield (%)	
		C ₂ H ₂	H ₂			C ₂ H ₂	C _m H _n	C ₂ H ₄	H ₂	C ₂ H ₆		C ₂ H ₄	C ₂ H ₆
2	229°	2.40	2.63	1.2	1.88	6	12	47	23	9	95	39	7
	229	2.36	2.63	1.2	2.04	11	11	40	27	8	90	38	8
	169	2.64	2.74	6.5	2.56	30	7	23	32	6	71	32	8
	169	2.71	2.77	6.3	2.72	32	7	21	32	5	68	32	7
	180	1.26	1.06	3.6	0.85	24	11	42	9	8	84	34	6
3	182	1.07	0.96	2.5	1.33	40	5	17	34	3	50	42	6

* See footnote to Table I.

reduction of nitric oxide. Thus acetylene and ammonia condense under a variety of conditions, though these are usually more vigorous than in the present work (see, *e.g.*, Berkman, Morrell, and Egloff, "Catalysis," 1940, p. 945).

Although the mechanism of the effect of nitric oxide is therefore uncertain, quite small amounts can clearly be adsorbed and react. Their influence is reminiscent of that of carbon monoxide, 2% or more of which is reported to retard acetylene removal and to raise the yield of liquid products considerably (Binnie, *J. Soc. Chem. Ind.*, 1931, **50**, 297).

(iv) *Effect of Oxygen*.—Less than *ca.* 10 mm. of air had little effect on reaction over nickel-pumice, but more than this amount (or its equivalent of oxygen alone) depressed the rate of fall in pressure at constant volume ($-dp/dt$), without, however, changing the general shape of the pressure-time curves; *i.e.*, no induction period or marked rise in $-dp/dt$ at any stage was found. The retardation increased with the amount of oxygen.

Table IV gives numerical data on this effect. In run 62, $-dp/dt$ was reduced to *ca.* one-fifth of its value in runs 59—61 by 54 mm. of air, and the retardation was almost as great in run 63, with no air admitted. In runs 64—66 (not shown), under the same conditions as run 63, $-dp/dt$ returned in stages to about that of runs 59—61. In the second group, 11.5 mm. of oxygen (run 36) depressed $-dp/dt$ to *ca.* one-quarter of its value in run 35, and 22 mm. (run 38) depressed it to *ca.* one-twelfth of that value. Recovery of the original rate was again spread over several runs.

The pressures in the gaseous product and yields in Table IV are maximum values, no products being supposed to condense before the gas is analysed. Inspection shows that when oxygen is added the resultants other than C₂ hydrocarbons must contain an unusually high proportion of hydrogen, which suggests water

TABLE IV.

Effects of air and oxygen on reaction.

Temp. = 83°. Each group of experiments over different samples of nickel-pumice (metal : pumice ratio 1 : 10).

Expt. no.	Initial press. (mm.)			Δp	<i>t</i>	Max. press. (mm.) in gaseous product.							Maximum yield (%)		
	H ₂	C ₂ H ₂	O ₂			C ₂ H ₂	C _m H _n	C ₂ H ₄	H ₂	C ₂ H ₆	O ₂	CO ₂	CO	C ₂ H ₄	C ₂ H ₆
59	400	206	—	206	22	63	10	60	237	13	—	—	—	42	9
60	395	203	—	202	23	63	12	56	237	14	—	—	—	40	10
61	397	198	—	200	21	61	11	55	242	13	—	—	—	40	9
62	400	203	54*	160	111	105	5	38.5	249	35	.2	3	2	39	35
63	400	200	—	299	193	4	12	73	139	59	—	0	—	37	30
35	298	302	—	301	28	94	13	78	94	13	—	—	—	38	6
36	302	299	11.5	300	108	110	14	76	74	28	0	2	2	40	15
37	302	300	—	300	35	93	13	82	83	21	—	—	—	40	10
38	300	301	22	304	324	132	12	68	49	47	1	3	3	40	28
39	297	300	—	301	62	96	15	80	65	35	—	2	2	38	17
40	299	302	—	301	39	97	16	81	76	25	—	—	—	39	12
41	300	302	—	300	31.5	93	17	78	83	19	—	2	1	38	9

* Air, not oxygen.

formation, since oxides of carbon will account for, at most, a small proportion of the oxygen removed. The yields of ethylene and ethane (but not their ratio) would then be lower than those tabulated. Their minimum values (estimated by assuming a water vapour pressure equal to twice the initial oxygen pressure) are, for run 62, 36% of ethylene and 33% of ethane, for run 36, 36% and 13%, and for run 38, 32% and 21%, respectively. The true yields will lie between these values and those in Table IV, since some oxygen is probably removed as oxides of carbon, and some almost certainly by combination with the catalyst, otherwise its effects would not extend to subsequent runs without oxygen, during which this inhibitor must be slowly removed from the nickel. If water is formed in such removal, small corrections to other yields will be necessary.

When these considerations are taken into account, there is no doubt that the yield of C_2 hydrocarbons, which in run 35 had its expected value for a catalyst not previously exposed to oxygen, is raised by oxygen. The increase is essentially in the ethane yield, and runs parallel with the retardation; as $-dp/dt$ increases again (*e.g.*, in runs 39—41) the ethane yield moves towards its value in unretarded runs. The yields of C_2 products in runs 59—61 are slightly larger than expected, probably because several runs with added air were included in nos. 47—58 of the same series.

It is clear that small amounts of oxygen are sufficiently strongly adsorbed to influence the reaction considerably, despite the strong adsorption of acetylene; the total inhibition of hydrogenation by oxygen, found with ethylene on nickel (Rideal, J., 1922, 121, 309), is not observed. Mechanisms can be suggested for the phenomena with acetylene, though definite conclusions cannot be reached. Thus the change of yield might be related to a lowering of surface concentration of acetylene by oxygen adsorption, the chance of two acetylene molecules combining being lowered; a lowering of acetylene adsorption in proportion to the fall in rate (*e.g.*, to $\frac{1}{5}$ — $\frac{1}{12}$ of its normal value), however, would probably make this chance very small, though much acetylene is still removed as products less volatile than C_2 hydrocarbons. Displacement of hydrogen may well also play a part, therefore, in the retardation. Another possibility is that oxygen is more strongly adsorbed at sites normally tending to favour polymerisation, than at others which normally favour the simple hydrogenation. The elevation of ethane production suggests that acetylene and ethylene are more nearly equally strongly adsorbed on the poisoned surface, possibly on account of a preference of oxygen for sites normally adsorbing acetylene, or some lattice modification induced by oxygen.

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