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Synthesis of Oxygenated Compounds from Carbon Monoxide and Hydrogen through Addition of Substituted Acetylenes

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The use of acetylenic compounds as the third component in the synthesis from CO and H_2 offered a means of obtaining aliphatic alcohols, aromatic alcohols, diols, and alkoxyalcohols as target products. These reactions over fused iron catalysts were found to belong to a new class of heterogeneously catalyzed reactions designated by the authors as "initiated hydrocondensation of carbon monoxide." The influence of some parameters on the specific features of the synthesis with the participation of the third component was studied.

Many researchers have studied the specific features of the course of the Fischer–Tropsch synthesis by introducing a third reactant phase component in addition to CO and H_2 (*1, 2*), using organic compounds of different classes as additives. An interesting result was obtained when acetylene was used as the third component in the synthesis of aliphatic alcohols (AA) on a fused iron catalyst (*3, 4*). More than 60% of the AA obtained in these experiments contained one molecule of the initial acetylene in their structure.

The present paper is devoted to further studies of the synthesis of oxygenated compounds on iron catalysts from carbon monoxide and hydrogen in the presence of substituted acetylenes of different structure.

EXPERIMENTAL

The syntheses from CO, H_2, and substituted acetylenes were carried out in a laboratory high-pressure installation, in a flow reactor. The catalyst employed in the experiments was a fused iron catalyst (1.6- to 2.5-mm fraction) prepared by fusing in an electric are a mixture of oxides having the following composition (mass %): Fe_3O_4, 96.51; K_2O, 0.50; N_2O, 0.25; CaO, 0.16; Al_2O_3, 1.98; V_2O_5, 0.37; SiO_2, 0.22; MgO–Cr_2O_3–CuO, 0.01 (overall), which was reduced with hydrogen at the temperature of 450°C and pressure of 50 atm. The surface of the reduced sample was 10.3 m^2/g (*5*).

The reaction products were analyzed by the method of gas-liquid chromatography on quartz capillary columns (L = 25 m, Carbowax-20M) and Chromato-mass spectrometry. Quantitative analysis was effected by the internal standard method. Analysis of the gases was carried out with the use of a steel packed column (L = 3 m, d = 3 mm, activated carbon).

RESULTS AND DISCUSSION

As the substituted acetylene—the third component in the synthesis from CO and H_2—phenylacetylene (PhA), which was added to the stream of the synthesis gas (a mixture of CO and H_2) with the aid of a metering device in the quantity of 0.35 mol%, at 160°C, 100 atm, $CO/H_2 = 1.5$, and a space velocity of the gas of 1000 h^{-1}, was used first.

Experimental data on changes in the degree of conversion of carbon monoxide prior to, in the course of, and after PhA supply are presented in Fig. 1. As is seen,

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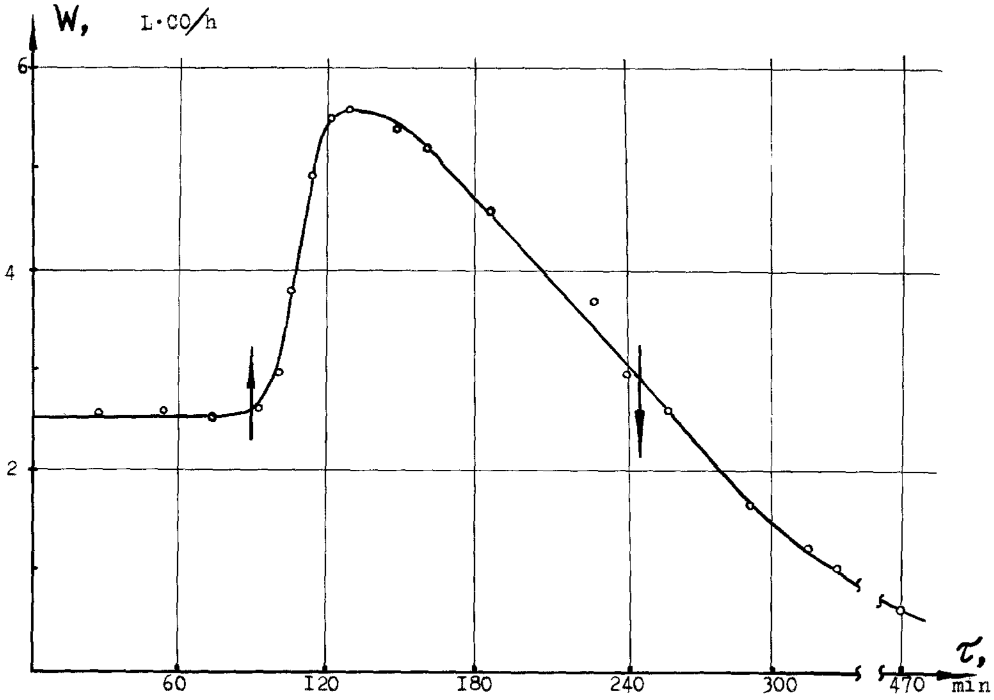


FIG. 1. Changes in the activity of fused iron catalyst with time. (↑) Commencement of PhA supply; (↓) end of PhA supply.

introducing PhA into the synthesis gas resulted in more than twofold increase in the conversion of carbon monoxide. In this case the liquid product of the synthesis contained, in addition to AA, C_1–C_{10}, i.e., products typical of these conditions, and also aromatic alcohols of the composition $Ph(CH_2)_nOH$, where $n = 3$–8. The aromatic alcohols thus produced were identified by the method of gas chromatography/mass spectrometry (GC/MS) (*6*).

Although the given result was reproduced many times within a wide range of parameters (150–190°C, 50–150 atm, $CO/H_2 = 0.5/2.0$), in all cases a rapid and irreversible decline of the carbon monoxide conversion was observed. More recently, it was established that the responsible factor was the side reaction of PhA oligomerization (*7*) which led to deactivation of the catalyst by the formed oligomers, blocking the active centers of the catalyst surface (*8*).

Carrying out experiments with the third component in the liquid phase, in the medium of benzene (*9*) made it possible to solve this problem, that is, to realize synthesis under stationary conditions. A characteristic feature of this synthesis is that prior to the start of the experiment a tubular reactor containing a catalyst bed was charged with benzene, the synthesis gas during the synthesis was bubbled from below, and the third component was supplied to the catalysis zone from above in the form of a 5–50% solution in benzene.

Comparative results of carrying out the synthesis of aromatic alcohols in the liquid-phase and gaseous-phase versions of the reaction are presented in Table 1.

As is seen from Table 1, the synthesis under liquid-phase conditions proceeds in a stable manner during a sufficiently long period of time. Moreover, in this case the activity of the catalyst, defined as the yield of the product in grams per liter of the catalyst, increases appreciably, whereas the

TABLE 1

Liquid-Phase and Gaseous-Phase Synthesis of Aromatic Alcohols

Synthesis	Efficiency in the synthesis of aromatic compounds with the participation of PhA (g aromatic compounds/liter · catalyst · h)			Efficiency in the synthesis of aliphatic compounds only from CO and H_2 (g aliphatic compounds liter · catalyst · h)
	Total	Alcohols	Hydrocarbons	Total
Liquid-phase	69[a]	48[a]	21[a]	1–2
Gaseous-phase	20[b]	15[b]	5[b]	6–8

Note. 150°C, 100 atm, $CO : H_2 = 1 : 1$, $V_g = 1000\ h^{-1}$ (flow CO + H_2 rates in liter (CO + H_2)/ liter · catalysts · h), $V_{PhA} = 0.45\ h^{-1}$ (flow PhA rates in liter · PhA/liter · catalyst · h).

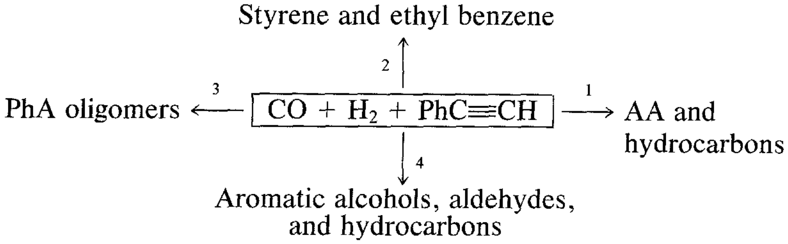
[a] Eighty hours of the catalyst operation without loss of activity.

[b] Determined during the first hour of PhA supply.

synthesis of AA proper from CO and H_2 proceeds with a lower activity.

A typical chromatogram of the product of synthesis of aromatic alcohols from carbon monoxide, hydrogen, and PhA is shown in Fig. 2. The following compounds were identified by GC/MS in the reaction products: AA and hydrocarbons C_1–C_8 of normal structure (products of the synthesis from CO and H_2); products of PhA hydrogenation: styrene and ethyl benzene; solvent: benzene; the unreacted PhA; the products of the target synthesis with the participation of PhA: aromatic hydrocarbons comprising a side chain C_3–C_8, predominantly of normal structure; aromatic aldehydes comprising a side chain C_3–C_7, of normal and isostructure; aromatic alcohols with a side chain C_3–C_8, of normal and isostructure.

As is seen, under the conditions of synthesis from CO, H_2, and the third component (PhA), the following conversions of the reaction mixture components may occur:



1. Synthesis of aliphatic compounds from CO and H_2.
2. PhA hydrogenation.
3. PhA oligomerization.
4. Synthesis from CO, H_2, and PhA.

The data on PhA conversion in the liquid-phase and gaseous-phase synthesis according to reactions 2–4 are given in Table 2. As is seen, under the conditions of liquid-phase synthesis the proportion of PhA participating in the formation of aromatic alcohols increases sharply, whereas the side reaction of PhA oligomerization practically does not go. This accounts for the increase

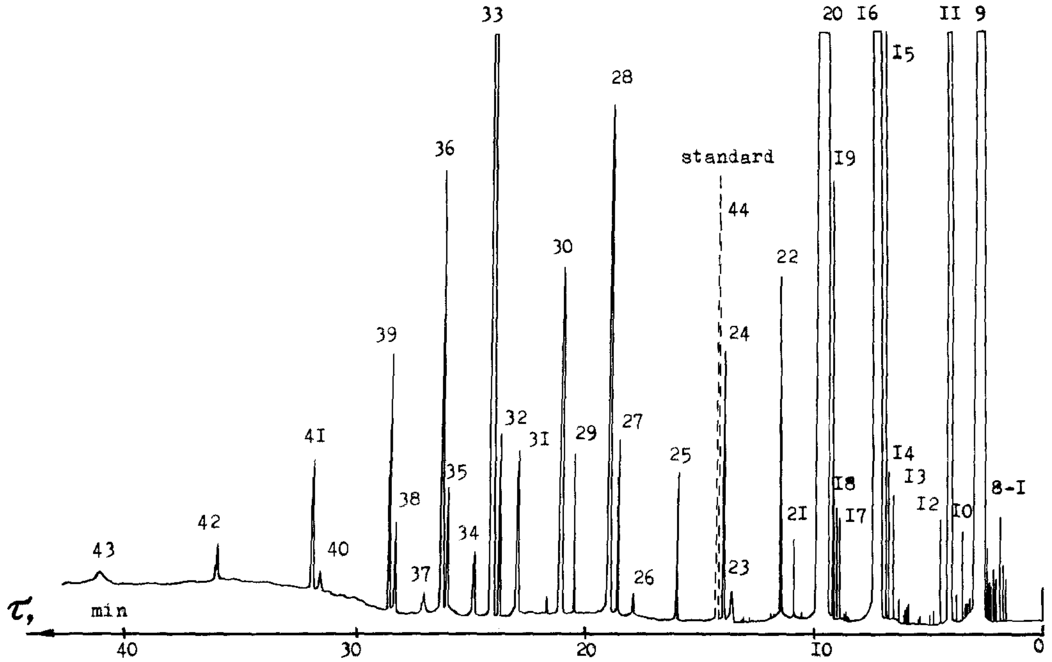


FIG. 2. Chromatogram of the product of liquid-phase synthesis of aromatic alcohols: (1) pentane; (2) hexane; (3) methanol; (4–6) not identified; (7) heptane; (8) octane; (9) benzene; (10) 1-propanol; (11) ethyl benzene; (12) 1-butanol; (13) 1-pentanol; (14) isopropyl benzene; (15) propyl benzene; (16) styrene; (17) 1-hexanol; (18) isobutyl benzene; (19) butyl benzene; (20) phenylacetylene; (21) 1-heptanol; (22) pentyl benzene; (23) 1-octanol; (24) hexyl benzene; (25) heptyl benzene; (26) octyl benzene; (27) 2-phenyl-propanal; (28) 3-phenyl-propanal; (29) 3-phenyl-butanal; (30) 4-phenyl-butanal; (31) 5-phenyl-pentanal; (32) 2-phenyl-1-propanol; (33) 3-phenyl-1-propanol; (34) 6-phenyl-hexanal; (35) 3-phenyl-1-butanol; (36) 4-phenyl-1-butanol; (37) 7-phenyl-heptanal; (38) 4-phenyl-1-heptanol; (39) 5-phenyl-1-pentanol; (40) 5-phenyl-1-hexanol; (41) 6-phenyl-1-hexanol; (42) 7-phenyl-1-heptanol; (43) 8-phenyl-1-octanol; (44) 2-ethyl-1-hexanol (standard).

in catalyst efficiency and operation stability.

Hydrocarbons, alcohols, diols, ethers, and halogenated compounds were used as the third component in the next stage of studying the syntheses from CO, H_2, and substituted acetylenes. The results of these experiments are presented in Table 3.

As is seen, 9 out of the 13 acetylene compounds introduced into the reaction from CO and H_2 (Nos. 1–9) participate in the synthesis, giving compounds listed in Table

TABLE 2

PhA Conversion in the Liquid-Phase and Gaseous-Phase Synthesis

Synthesis	PhA conversion (%)	Proportion of PhA participating in reaction No (mass %)			Unreacted PhA (mass %)	Losses (mass %)
		4	2	3		
Liquid-phase	71	21	43	1	29	6
Gaseous-phase	95	7	15	70	5	3

Note. 150°C, 100 atm, $CO:H_2 = 1:1$, $V_g = 1000\ h^{-1}$, $V_{PhA} = 0.45\ h^{-1}$.

TABLE 3

Syntheses from CO and H_2 with the Participation of the Third Component

Acetylene compound	Main products of synthesis	T (°C)	P (atm)	CO/H_2	Catalyst efficiency/CO conversion (g/liter · h/liter CO/h)		α
					In the synthesis from CO and H_2	In the synthesis with alkyne	
1. $HC\equiv CH$[a]	AA C_3–C_{25}	180–190	100–200	1	35–55/–	310–450/–	0.35
2. $PhC\equiv CH$	Aromatic Alcohols C_9–C_{14}	155	75	0.56	3.5–4/4.5	75/27–28	0.45
3. $CH_3(CH_2)_5C\equiv CH$	AA C_9–C_{20}	160	100	1	4–4.5/5–7	110/36–37	0.39
4. $C_2H_5C\equiv CC_2H_5$	AA C_7–C_{25}	160	100	1	4–4.5/5–7	100/40–41	0.39
5. $HOCH_2C\equiv CH$	α,ω-diols C_4–C_{10}	170	100	1	6–8/8–10	35/12–13	0.24
6. $HOCH_2CH_2C\equiv CH$	α,ω-diols C_5–C_{10}	170	150	0.5	8–10/10–12	28/11–12	0.24
7. $CH_3OCH_2C\equiv CH$	Methoxyalcohols C_5–C_9	150	100	1	2.5–3.5/3–4	49/18–20	0.31
8. $(CH_3)_3COCH_2C\equiv CH$	Tert-butoxyalcohols C_8–C_{11}	150	100	1	2.5–3.5/3–4	36/13–14	0.31
9. $PhCH_2OCH_2C\equiv CH$	Benzoxyalcohols C_{11}–C_{12}	170	100	1	6–8/8–10	66/8–10	—
10. $CH_3OC\equiv CH$			Reaction does not go				
11. $C_2H_5OC\equiv CH$			Reaction does not go				
12. $HOCH_2C\equiv CCH_2OH$			Reaction does not go				
13. $HalCH_2C\equiv CH$			Reaction does not go				

[a] Data are borrowed from Loktev, S. M., *J. Mol. Catal.* **17,** 225 (1982).

3. Thus, the participation of an acetylene compound in the synthesis from CO and H_2 implies that this molecule is incorporated once into the growing chain. The products formed constitute a homologous series of compounds, comprising the initial substituted acetylene (without the triple bond) which, with the help of several CH_2 groups, is connected with the newly formed functional group.

The distribution of the molecular weights of the resulting compounds obeys the well-known Schultz–Flory equation, the distribution typical for the products of the Fischer–Tropsch synthesis. The distribution parameter, α—the chain growth parameter— varies within 0.24–0.45; it practically does not depend on the conditions under which the reaction is conducted, but it is dependent on the nature of the third component employed. The introduction of acetylene compounds into the synthesis from CO and H_2 leads to an increase in the catalyst activity: the efficiency of the catalyst in terms of the synthesis products grows, the CO conversion increases.

When diethylacetylene (No. 4) was introduced into the synthesis, the expected iso-compounds were absent in the reaction mixture, but the composition of the reaction products points to an increased quantity of alcohols C_7–C_{24} (the ratio of alcohols C_7/C_6 in the synthesis without diethylacetylene is 0.81–0.72, whereas in the synthesis with diethylacetylene it is 8.5; the situation is similar for all alcohols C_{7+}). This suggested isomerization of diethylacetylene into 1-hexyne, which entered into synthesis with carbon monoxide and hydrogen, giving alcohols C_7–C_{24}, predominantly of normal structure (similar to 1-octyne (No. 3)).

We should like to note that the benzyl ether of propargyl alcohol displayed a low activity in the synthesis with the participation of CO and H_2, the conversion of carbon monoxide practically did not increase, and the synthesis products contained only one or two methylene groups formed from CO and H_2.

The negative result with the rest of the acetylene compounds (Nos. 10–13) is, in our opinion, due to different reasons. In particular, alkoxyacetylenes are unstable compounds; that is, they could become decomposed prior to entering into the reaction. Butyndiol differs from all other compounds in that it entered into the reaction only with hydrogen and underwent conversion only in direction 2 (the scheme, showed previously), forming 2-butene-1,4-diol, and 1,4-butanediol. Such a result, in combination with the data on diethylacetylene, gave grounds to suppose that disubstituted acetylenes cannot enter into the synthesis with the participation of carbon monoxide and hydrogen.

Finally, propargyl halides deactivated the catalyst rapidly and irreversibly. According to the ultimate analysis data, the catalyst discharged after the experiments with propargyl halides contained an insignificant quantity of carbon (less than 0.5 mass %), whereas the halide content was high (16–19.5 mass %). These data indicate that under the synthesis conditions propargyl halides may be hydrolyzed and given hydrogen halides; the latter interact with the catalyst and form stable, catalytically inactive iron halides.

Thus, the data obtained indicate that monosubstituted acetylenes, stable under the synthesis conditions, interact with carbon monoxide and hydrogen in the following manner:

$$zR\text{–}C{\equiv}CH + xCO + yH_2 \rightarrow R - (CH_2)_nOH + R - (CH_2)_{n-1}CHO + R - (CH_2)_{n-1}CH_3.$$

The data on the influence of the contact time of the reaction mixture on the composition of the products of this reaction are listed in Table 4. Using these data, we have determined the changes in the relative selectivities γ: alkoxyalcohol/alkoxyaldehyde (γ_1), aromatic hydrocarbon/aromatic aldehyde (γ_2), and aromatic alcohol/aromatic aldehyde (γ_3).

As is seen in Fig. 3, in all three cases when $\tau \rightarrow 0$, the relative selectivities γ_i tend to zero. This means that the primary products of conversion of CO, H_2, and monosubstituted acetylenes are aldehydes, while alcohols and hydrocarbons are products of secondary conversions.

Studies of the influence of some parameters on the specific features of the course of the synthesis with the participation of the third component (Table 5) revealed that at 110–130°C, 50–100 atm, $CO/H_2 = 1$, the only products of the synthesis are com-

TABLE 4

Composition of the Products of Synthesis (mass %) of Aromatic Alcohols from CO, H_2, and PhA (I) and of alkoxyalcohols from CO, H_2, and Tert-butyl Ether of Propargyl Alcohol (II)

Space velocity (h^{-1})	Contact time (h)	II		I		
		Alkoxyalcohols	Alkoxyaldehydes	Aromatic		
				Hydrocarbons	Alcohols	Aldehydes
0.30	3.33	50	50	35	40	25
0.58	1.72	—	—	35	30	35
0.70	1.43	45	55	—	—	—
1.1	0.91	40	60	—	—	—
1.33	0.75	—	—	30	25	45
1.50	0.67	35	65	30	20	50
1.87	0.53	—	—	25	20	55
2.20	0.45	25	75	—	—	—
2.94	0.34	—	—	20	10	70
3.33	0.30	10	90	—	—	—

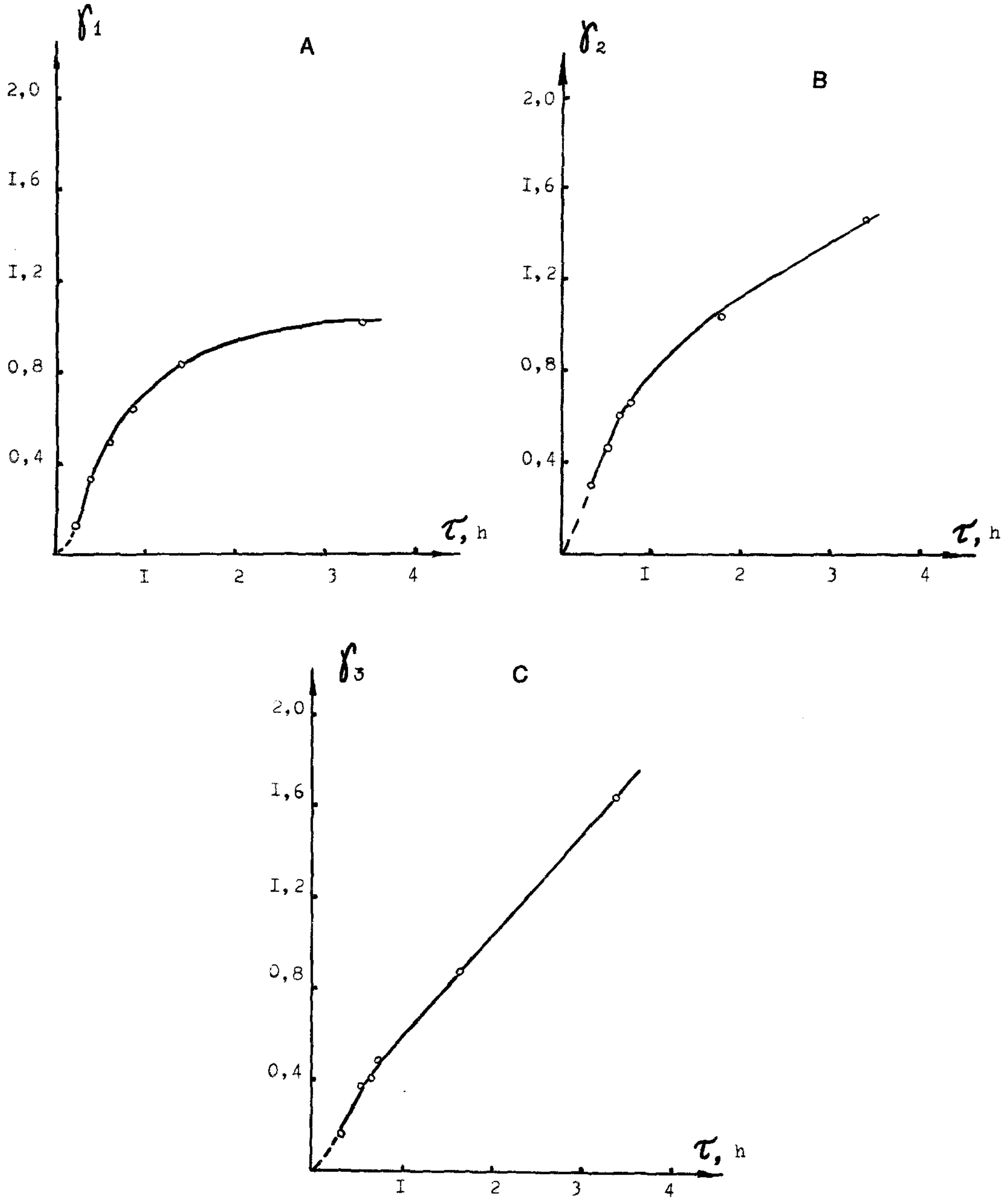


FIG. 3. Relative selectivity vs contact time dependence curves: γ_1 (A), γ_2 (B), γ_3 (C).

pounds containing a fragment of the initial monosubstituted acetylene in their structure. In other words, under the conditions when proper conversions of CO and H_2 do not occur (AA and hydrocarbons are absent), the synthesis with the participation of the third component may still proceed with a sufficiently high rate.

These data allow us to assert that monosubstituted acetylenes play the role of an initiator in the syntheses from CO and H_2 and to pool the reactions studied by us un-

TABLE 5

The Influence of Temperature and Pressure on the Synthesis from Carbon Monoxide, Hydrogen, and the Third Component

Third component	T (°C)	P (atm)	Catalyst activity in the synthesis	
			With alkyne (liter CO/liter · h)	Only from CO and H_2 (liter CO/liter · h)
$PhC{\equiv}CH$	110	50	3–3.5	0
$PhC{\equiv}CH$	130	50	7.7–9	0
$PhC{\equiv}CH$	170	50	18–20	12–15
$(CH_3)_3COCH_2C{\equiv}CH$	120	100	5.5–7	0
$(CH_3)_3COCH_2C{\equiv}CH$	150	100	13–14	3–4
—	130	50	—	0
—	150	100	—	3–4

der one common name, "initiated hydrocondensation of carbon monoxide."

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