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HYDRIDES OF GERMANIUM

J. E. Drake and W. L. Jolly

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J.E. Drake and W. L. Jolly

Department of Chemistry and
Lawrence Radiation Laboratory,
University of California,
Berkeley, 4, California

ABSTRACT

Monogermane has been prepared by the reduction of aqueous germanate solutions with hydroborate, and higher germanes - up to nonagermanes - have been prepared by the decomposition of monogermane in an ozonizer-type silent electric discharge. The higher germanes were separated by gas-liquid chromatography and they were identified by their vapor pressures, infrared spectra, mass spectra, and proton magnetic resonance spectra.

HYDRIDES OF GERMANIUM

The first extensive study of germanium hydrides was made by Dennis and his coworkers[1] who prepared mono-, di-, and trigermane by the acid hydrolysis of magnesium germanide. By a similar method, Amberger[2] has prepared tetra- and pentagermanes. Monogermane has been prepared from the reduction of germanic acid or germanium chloride solutions by lithium aluminium hydride,[3] by lithium tri-tertbutoxyalumino hydride,[4] and by hydroborate solutions.[5]

Schwarz and Heinrich[6] obtained di- and trisilane by passing monosilane through an ozonizer type electric discharge. Diborane[7] was decomposed to higher hydrides, and arsine[8] was decomposed to diarsine by a similar electric discharge system but the technique had not been tried for monogermane. We have prepared monogermane in good yield by the reduction of aqueous alkaline germanate solutions and we have prepared germanes - up to nonagermanes - by the decomposition of monogermane in an electric discharge.

Experimental

1. Studies of Aqueous Germanate Solutions

Mono-, di-, and trigermane were prepared by the slow addition of an alkaline solution of potassium hydroborate and germanium dioxide to an acidic medium. A current of oxygen-free nitrogen was used to sweep the hydrides from the reaction vessel as they were formed. The hydrides were condensed out in traps surrounded by liquid nitrogen and were subsequently separated and purified by distillation in vacuo. With sulphuric acid a large amount of foaming occurred. The foaming could be reduced by adding about 1% of a polyglycol, but larger amounts of hydroborate were then needed to give comparable yields. A large amount of yellow-orange residue was formed during the reaction. This residue was identified from its decomposition products and from its infrared spectrum (KBr pellets) as a polymeric germane $(GeH)_x$.[9] The yield of monogermane was not improved when the concentration of the sulphuric acid was changed or when hydrochloric acid was used. With glacial acetic acid practically no foaming occurred, very little residue was formed, and the yields of mono- and digermane were improved.

In Fig. 1, the yields of monogermane and digermane (based on the amount of germanium in solution) are plotted against the ratio of hydroborate to germanate in the alkaline solution. Plots are shown for the addition of the alkaline solution to glacial acetic acid and to sulphuric acid. The best results were obtained with a ratio of $BH_4^-/Ge(IV)$ of about three when the yields, based on the amount of germanium dioxide, were monogermane 73% and digermane 9%. Trigermane was more easily recovered from the sulphuric acid system, but the yield was never greater than 2.5%.

2. Studies of the Effect of Electrical Discharges on Monogermane

a. The low pressure system. The apparatus is shown in Fig. 2. The flow of monogermane from reservoir A-into the reaction vessel was controlled by the needle value,V, and the pressure was determined by the dibutyl phthalate manometer M. The ozonizer was surrounded by a cold-bath containing an acetone-dry ice-hydrochloric acid mixture which was grounded. The inner finger, filled with the same cooling mixture, was connected to a high voltage a.c. supply. Higher germanes were condensed in the ozonizer, and mono- and digermane were condensed in traps B, C, and D, which were at liquid nitrogen temperature. Hydrogen was pumped out continuously through stopcock 1. Consecutive runs under the same conditions of voltage, pressure and flow-rate gave similar results, even when the ozonizer was not cleaned between each run. The conditions were varied to give voltages from 4 to 15 kv, pressures from 0.5 to 5.0 cm of dibutyl phthalate, and flow-rates from 0.025 to 25.0 mmoles of monogermane per minute. Figure 3 shows the percentage decomposition of monogermane and the percentage yield of digermane - based on the monogermane decomposed - for different flow-rates, at two conditions of constant voltage and pressure. The best conditions - high voltage, high pressure, and medium flow-rates - gave digermane in 55% yield and trigermane in 10% yield. Because the percentage conversion was low, only 1mmole of digermane and about 0.1 mmole of trigermane were obtained from the passage of 100 mmoles of monogermane.

b. The high pressure system. The apparatus was altered to a closed system in which the monogermane was at a pressure of about 30 cm. of mercury. A Toepler pump was used to circulate the monogermane, and the amount of the monogermane to be decomposed could be varied by changing the size of a reservoir. The ozonizer was still kept at -78°C and the discharge was run for various lengths of time. The amount of monogermane was measured both

before and after each run. Hydrogen was not pumped out until the end of a run and so the change in the pressure gave an indication of the extent of the decomposition of the monogermane according to

$$GeH_4 \longrightarrow \text{"}GeH_x\text{"} + (4-x)/2\ H_2$$

(In most runs x was from 2.0-2.5.)

Table 1 shows the percentage decomposition of monogermane and the percentage yields of di-, tri-, and tetragermane for different conditions of voltage, pressure and time. Under the best conditions 8 mmoles of both di- and trigermane were obtained from 100 mmoles monogermane in about an hour.

3. Studies of the Effect of Heat on Monogermane

In these experiments the ozonizer was replaced by a heated tube. In the low-pressure system the yields were about half as great as those from the corresponding ozonizer system. In the high-pressure system it was impossible to get yields of di-, and trigermane greater than 3%.

4. The Separation and Identification of the Germanes

a. Separation. The boiling points of mono-, di-, and trigermane are sufficiently far apart to allow their separation by fractional condensation in the usual vacuum-line apparatus. Distillation through traps cooled to -33°C, and -63°C, and -112°C removed tetra-, tri-, and digermane, respectively.

The other hydrides were separated by gas-liquid chromatography on columns containing 10% of silicone fluid on Celite.[10] By varying the flow rate of the helium carrier gas and the temperature of the column, many peaks could be resolved.

A list of the retention times for various conditions is given in Table 2. The two isomers of tetragermane and the pentagermanes were collected from the

column by a technique similar to that described by Simmons and Kelley.[11]

b. Identification. Mono- and digermane were characterized by their vapour pressures and infrared spectra - the spectra were recorded on a Perkin-Elmer Infracord Spectrophotometer, model 137. The infrared spectra and the mass spectra of tri-, n-tetra-, and iso-tetragermane, and of a mixture of the pentagermanes were obtained. The proton magnetic resonance spectra of three of the germanes are shown in Fig. 4. The spectrum of digermane gave the chemical shift for $-GeH_3$ as 3.4 ppm to lower field of tetramethylsilane as external standard. All spectra were recorded on a Varian, model A-60, NMR Spectrometer.

DISCUSSION

1. Preparation

The preparation of monogermane that we have described is an extremely useful one because the germane can be obtained pure in a short time and high yields are obtained with small excesses of hydroborate, see Fig. 1. We found that the yield of monogermane is gradually lowered as the excess of the reducing agent is increased beyond threefold. Sujishi and Keith[4] reported a similar result with lithium tri-tertbutoxyaluminohydride as the reducing agent. Although the yield of monogermane is lowered, the amount of germanium (IV) that is reduced continues to rise, because large quantities of the polymeric hydride $(GeH)_x$ are now formed.

Undoubtedly the best method for preparing higher germanes is by the decomposition of monogermane in a high pressure discharge system. In experiments carried out at -78°C, see Table 1, the percentage yields of tri- and tetragermane remained constant with time but the percentage yield

of digermane was lowered. The vapour pressure of digermane is high enough at -78°C for some of it to be decomposed but the higher germanes are frozen out as they are formed. Similarly trigermane is not frozen out completely at 0°C and so some of it was decomposed and the yields were smaller. The importance of rapid condensation explains to some extent the poor yields in the pyrolysis experiments. If the ozonizer was kept at room temperature and the cold trap was placed some distance beyond the ozonizer to delay the condensation of the higher germanes, much better yields were obtained than from the pyrolysis experiments, although the yields were much lower than those when the ozonizer was at -78°C. Thus it seems that the excitation of monogermane by an electrical discharge is intrinsically a better method for bringing about polymerisation.

2. Separation and Identification

Trigermane was identified by its vapour pressure and its mass spectrum. Its proton magnetic resonance spectrum (see Fig. 4a) was recorded using pure trigermane. The spectrum is very similar to that of trisilane[12] and both spectra are almost mirror images of that of propane.[13] The three spectra are characterized by a small ratio of chemical shift to spin-spin coupling constant for the protons in $-MH_2-$ and $-MH_3$, (M = C, Si, Ge.) By a comparison with the spectrum of trisilane, the positions of the center of the $-GeH_3$ triplet and the $-GeH_2-$ septet can be assigned to the peaks 'x' and 'y' respectively. The resonance field for $-GeH_3$ in trigermane is 3.3 ppm lower than that of tetramethylsilane (as an external standard). (The corresponding shift for $-SiH_3$ in silanes is about 3.3 to 3.6 ppm and for $-CH_3$ in propane is 1.1 ppm, both toward lower field from tetramethylsilane).

The internal chemical shift from $-GeH_3$ to $-GeH_2-$ is 0.193 ppm to higher

field. The corresponding shift in trisilane is 0.167 ppm also to higher field, and in propane it is 0.438 ppm to lower field. A simple, but by no means complete, explanation of the differences in the spectra can be given on the basis of the relative electronegativities of carbon, germanium, hydrogen, and silicon. The order of the electronegativities is C > H > Si $\cong$ Ge. When an H atom of a $-CH_3$ group is replaced by a C atom, the electron density around each of the remaining protons is lowered and the proton resonance occurs at a lower field. On the other hand, when an H atom of either an $-SiH_3$ or $-GeH_3$ group is replaced by an Si or Ge atom, respectively, the electron density around the remaining protons is increased and the resonance occurs at a higher field.

The infrared spectra of tri-, n-tetra-, and iso-tetragermane are so similar that they only identify them as being germanium hydrides. On the basis of expected relative volatilities, we assumed that n-tetragermane was held longer on the chromatographic column than iso-tetragermane. A comparison of the mass spectra of the two fractions with the mass spectra of n- and iso-butane agreed with this assumption. The mass spectrum of the isomer, presumed to be n-tetragermane, had a fragmentation pattern similar to that of n-butane, in that the relative amounts of the gragments were in the order, $M_3^+ > M_2^+ > M_4^+ > M_1^+$ (M = Ge or C). The other isomer, presumed to be iso-tetragermane, had a fragmentation pattern similar to that of iso-butane, the order being $M_3^+ > M_2^+ > M_1^+ > M_4^+$. The proton magnetic resonance spectrum of the n-tetragermane (see Fig. 4b) is similar to that of n-butane in that no easily explained pattern is seen. The spectrum of iso-butane consists of a series of equally spaced lines, that are preseumed to be part of a series of 10, and a strong symmetrical doublet with the same spacing. The spectrum of iso-tetragermane (see Fig. 4c) was taken in a very

dilute solution of n-hexane and it consisted of a symmetrical doublet. The series of ten lines caused by the splitting of the (=GeH-) hydrogen was presumably too weak to be seen under these circumstances. From the spacing of the doublet the spin-spin coupling constant $J_{GeH,\ GeH_3}$, is 4 cycles/sec. (J_{CH,CH_3}, is 5 cycles/sec.) The chemical shift of $-GeH_3$ in iso-tetragermane is 3.4 ppm to lower field referred to tetramethyl silane. The yield of n-tetragermane was from four to ten times that of the iso-form. (In making this estimation of yields we assumed that the two species were equally sensitive to detection by our thermal conductivity cell, and so we may be underestimating the yields of the branched species. In the alkanes the sensitivities decrease in the order of straight-chain alkanes > dimethylalkanes>trimethylalkanes>monomethylalkanes>tetramethylalkanes, and also all alkanes of a given degree of branching have the same sensitivity irrespective of carbon number.) Nevertheless, the relative yields were those that might be expected if, in the discharge tube, tetragermane is built up from Ge_1 units plus Ge_3 units and, possibly, pairs of Ge_2 units.

The pentagermanes were collected as a group from the chromatographic column. The infrared spectrum confirmed that there were germanium hydrides and the mass spectrum confirmed that they were pentagermanes. The peaks were assigned on the basis of the expected relative retention times of the three isomers on the chromatrographic column, comparisons were made with tables of the retention times of hydrocarbons on silicone columns, and we assumed that the isomers would emerge in the order neo-, iso-, n-pentagermane. The relative yields of these isomers - based on the areas under the peaks - are remarkably close to those predicted on the basis of a statistical build-up.

By similar arguments the four peaks of the hexagermanes may be tentatively assigned as follows: A = 2,2-digermyltetragermane; B = 2,3-digermyltetragermane; C = a mixture of 2-germylpentagermane and 3-germylpentagermane; D =

n-hexagermane; (germyl = GeH_3).

This type of assignment (already hazardous with the hexagermanes) is impossible with the heptagermanes; but it is probable that K is the normal species. For the normal series of hydrocarbons, a plot of the logarithm of the retention time against the number of carbon atoms per molecule gives a straight line.[14] This is also true for the silanes[15] and the germanes.[10]

The relative yields of the isomers varied for each preparation, but for hexa- and heptagermanes, and sometimes for pentagermanes, the normal species was never the most abundant, which result is to be expected from statistical considerations. Typical yields of the isomers, calculated from the peak areas and based on the amount of germanium in monogermane that was converted, were as follows: pentagermanes 0.8%, hexagermanes 0.3%, heptagermanes 0.3%, octagermanes 0.05%, and nonagermanes less than 0.01%.

We thank Dr. J. J. Turner for his help in the discussion of the proton magnetic resonance spectra and for the use of his thesis for making our comparisons with the spectra of trisilane and propane.

Table 1

Results from the high pressure discharge system, with the ozonizer at -78°C

Voltage (kv)	Pressure (cm Hg)	Time (hours)	% decomposition of GeH_4	% Yield Ge_2H_6	Ge_3H_8	Ge_4H_{10}
10	10	2.0	94.5	8.0	30.0	-
10	20	1.0	19.3	38.6	26.0	9.5
[a]10	20	1.0	8.0	25.9	19.2	10.9
[b]10	20	1.0	52.7	14.6	9.8	9.9
10	20	2.0	84.0	25.4	26.9	8.9
10	20	3.0	86.9	28.6	26.1	8.6
[a]10	20	3.0	67.5	5.1	6.3	8.9
10	20	3.5	91.1	11.5	-	-
10	20	5.5	95.2	12.0	30.0	-
10	30	2.0	75.2	34.8	26.8	-
10	30	5.5	95.0	26.7	29.7	-
15	20	2.0	93.8	26.5	28.1	-
15	30	2.0	94.8	26.6	26.6	-
15	40	5.5	88.4	39.0	31.8	12

[a] Ozonizer at 0°C.

[b] Ozonizer at 25°C, with another cold trap at -78°C in the system.

Table 2

Retention Times at Various Temperatures (in minutes)

Species	Flow: 60 c.c./minute				Flow: 88 c.c./minute				
	95°	125°	150°	190°	110°	145°	160°	170°	190°
Ge_3H_8	1.0	0.55	-	-	0.55	~0.35	-	-	-
iso-Ge_4H_{10}	2.9	1.5	1.0	0.5	1.5	0.8	0.8	0.6	~0.45
n-Ge_4H_{10}	3.5				1.7	0.9			
neo-Ge_5H_{12}	6.4	2.5	1.3	-	3.2	1.5	1.3	-	-
iso-Ge_5H_{12}	9.4	3.4	2.0	1.1	4.5	2.0	1.7	1.2	0.95
n-Ge_5H_{12}	13.5	4.0	2.2		5.5	2.4	1.9	1.4	
Ge_6H_{14}[s] A	-	-	3.6	1.6	9.0	3.8	2.6	2.0	1.5
B	-	-	3.9		11.3	4.8	3.4	2.5	1.9
C	-	9.0	4.4	1.9	13.5	5.2	3.7	2.7	
D	-	12.0	5.2	2.2	17.5	6.6	4.5	3.4	2.2
Ge_7H_{16}[s] E	-	-	-	-	-	-	-	4.0	2.6
F	-	-	6.5	-	-	10.0	6.7	4.8	3.1
G	-	-				10.2			
H	-	-	7.9	2.9	-	12.0	7.6	5.4	3.4
I	-	-	8.8	3.4	-	15.0	8.8	6.3	4.0
J	-	-	11.0	4.0	-	18.0	10.5	7.8	4.8
K	-	-	15.0	4.7	-	18.6	10.8	8.0	
Ge_8H_{18}[s]				7.0 → 11.0					6.5 → 10.0
L									7.5
M									8.5
Ge_9H_{20}[s]				14 → 20					13.5 → 20

Table 3

Principal Peaks in Infrared Spectra of Tri-, Tetra-, and Pentagermanes

	Vibrations (cm^{-1})		
	Ge-H stretching	Ge-H bending	
Ge_3H_8 [a]	2080 (m.s.)	796 (s)	880 (w)
n-Ge_4H_{10}	2045 (m.s.)	792 (s)	860 (w)
iso-Ge_4H_{10}	2060 (m.s.)	784 (s)	-
Ge_5H_{12} [a]	2080 (m.s.)	795 (s)	860 (w)
$(GeH)_x$ [a]	2060 (m.s.)	775 (s)	832 (s)

s - strong

m.s. - medium-strong

w - weak

[a] These spectra are recorded in an earlier report. Subsequently Emeleus and Mackay[16] have reported the positions of the principal peaks of trigermane which agree with our figures.

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FIGURE LEGENDS

Fig. 1. Yields of monogermane and digermane (based on the concentration of GeH_4)

(A) Yield of GeH_4 using glacial acetic acid.

(B) Yield of GeH_4 using sulphuric acid.

(C) Yield of Ge_2H_6 using glacial acetic acid.

(D) Yield of Ge_2H_6 using sulphuric acid.

Fig. 2 Apparatus for the low-pressure discharge system.

Fig. 3 Percent Decomposition of GeH_4 and Percent Yield of Ge_2H_6 (Ozonizer at -78°)

(A) Percent yield of Ge_2H_6 at 8kv and 2 cm. Hg.

(B) Percent yield of Ge_2H_6 at 15kv and 4.5 cm. Hg.

(C) Percent decomposition of GeH_4 at 8kv and 2 cm. Hg (●) and at 15 kv and 4.5 cm Hg (■).

Fig. 4 Proton magnetic resonance spectra of a) trigermane, b) n-tetragermane, and c) iso-tetragermane. (In ppm referred to an external sample of tetramethylsilane.)

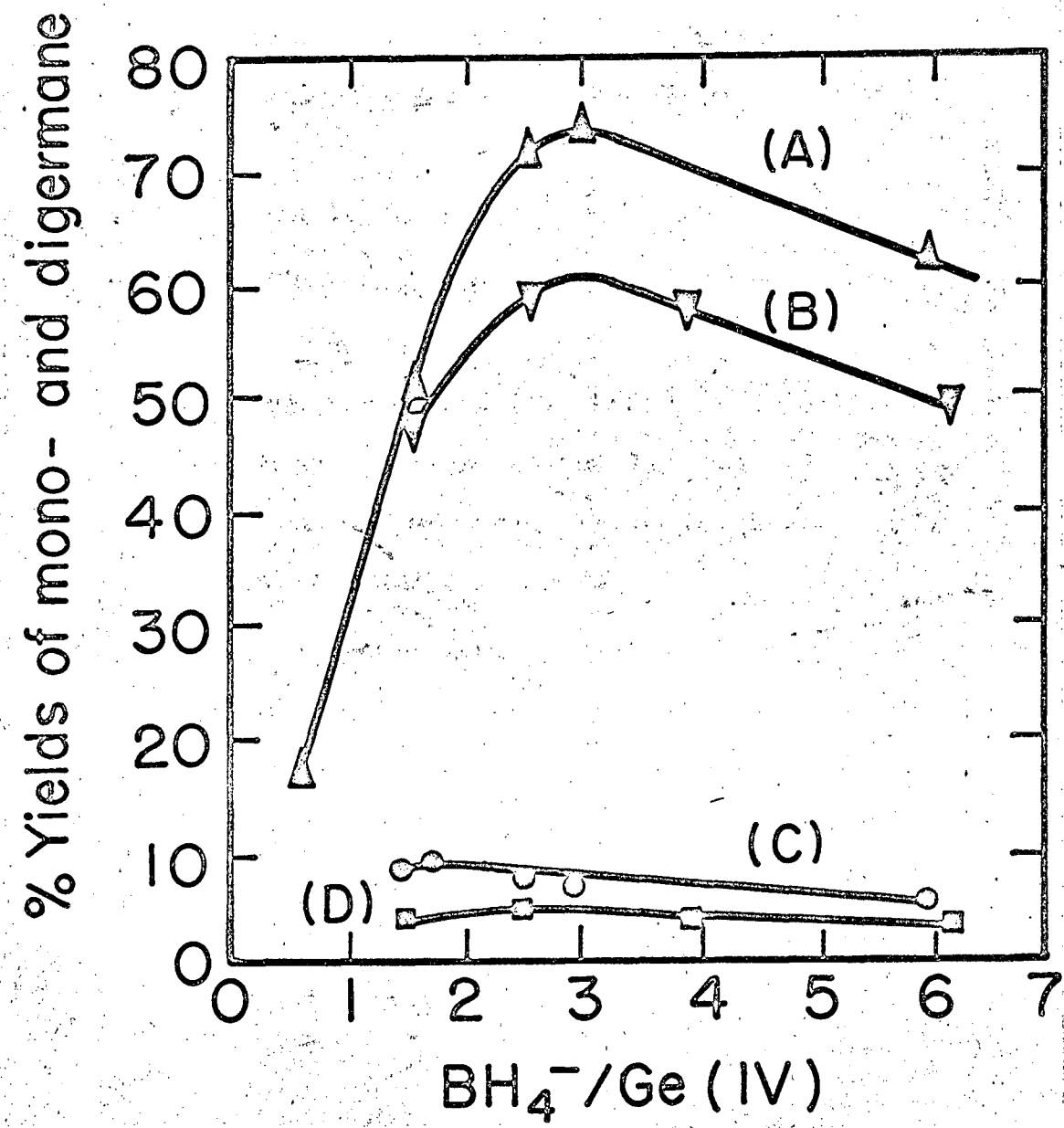

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Fig. 3

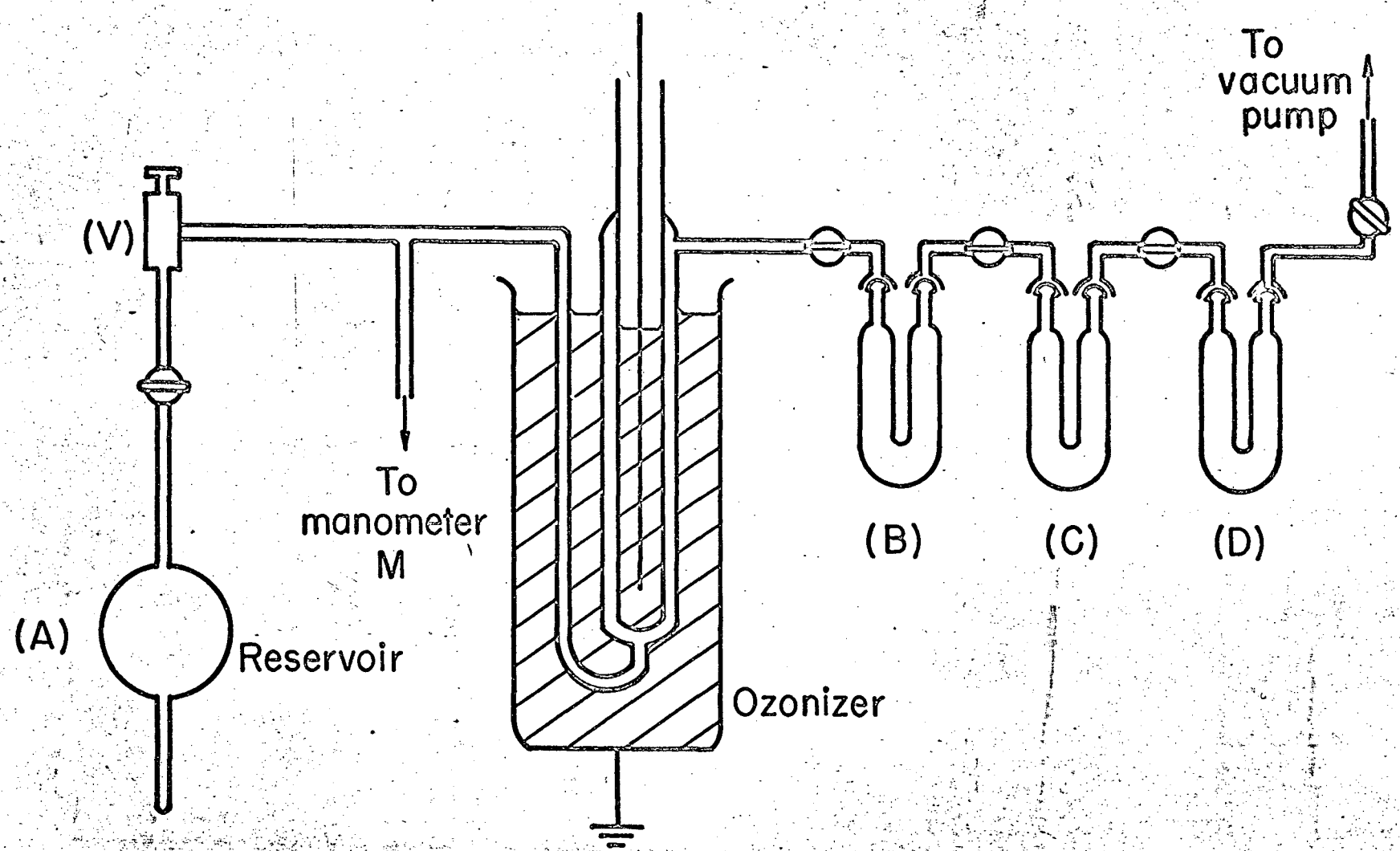

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Fig. 2

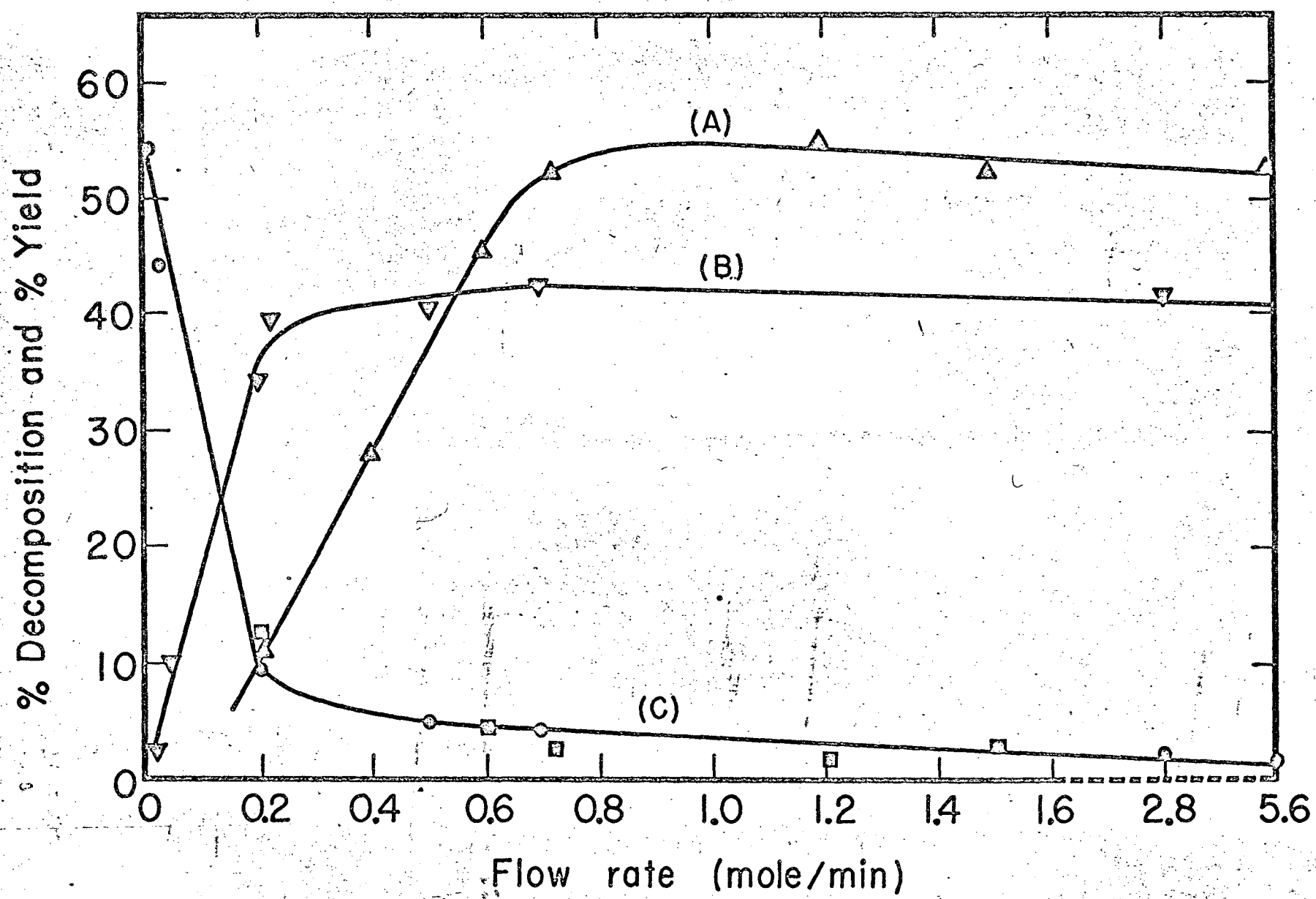

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Fig. 3

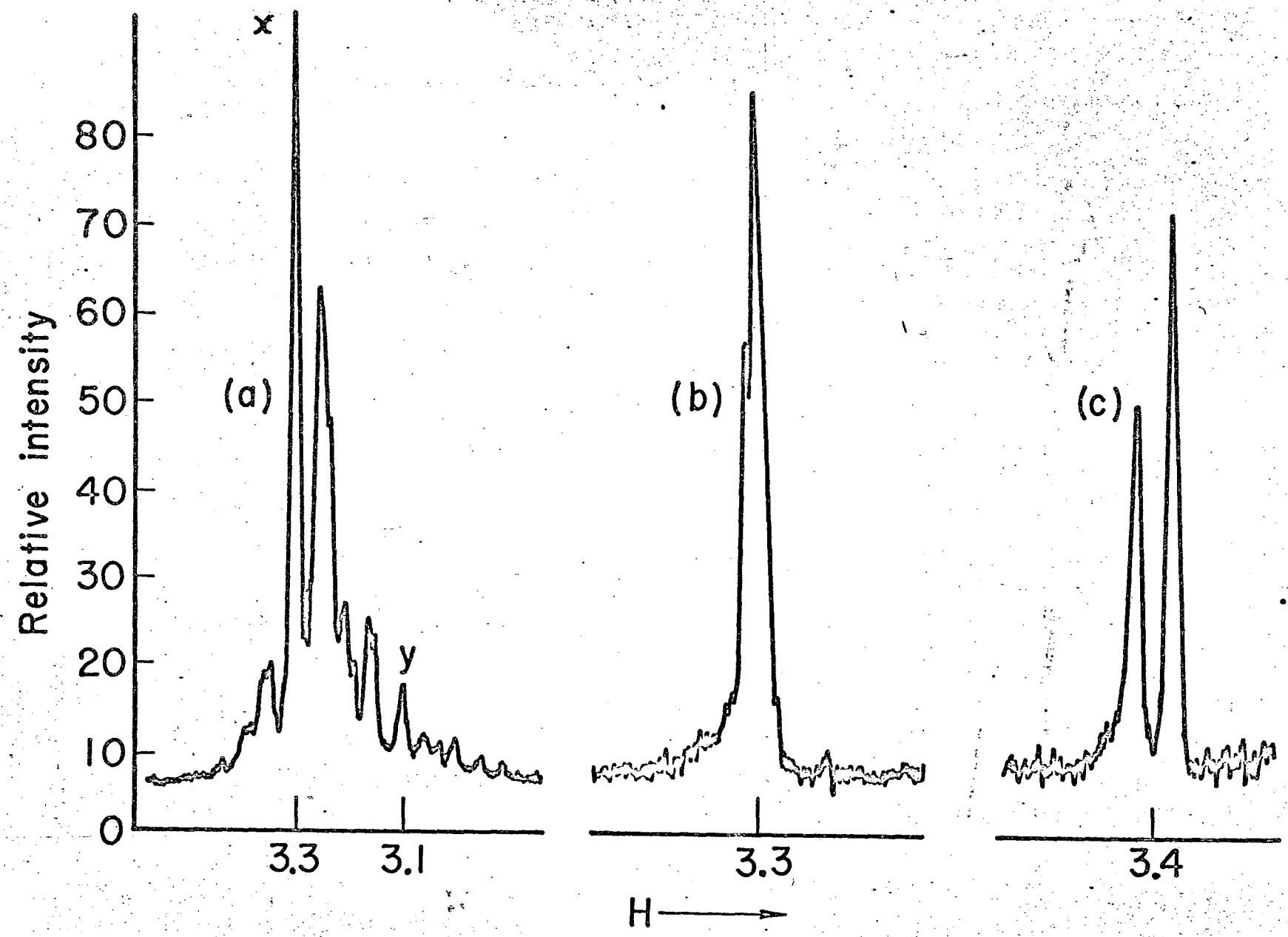

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Fig. 4