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The Hydrogenation of Acetylene

IV. The Reaction of Acetylene with Deuterium Catalyzed by Alumina-Supported Rhodium, Palladium, Iridium, and Platinum

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The reaction of acetylene with deuterium has been studied using alumina-supported Rh (134–200°), Pd (0–46°), Ir (30–120°), and Pt (50–110°). Products have been analyzed by mass and infrared spectrometry. No acetylene exchange was observed; hydrogen exchange was fairly rapid over Rh and Ir, slow over Pt, and negligible over Pd. All possible isotopic ethylenes were formed. Ethylene-d_2 was usually most abundant, but its yield varied from metal to metal ($Pt > Pd > Ir > Rh$), and over each metal the fraction that it formed of the total ethylene yield increased with increasing initial deuterium pressure and fell with increasing temperature. When the yield of ethylene-d_2 was high (as over Pd and Pt) its major component was the *cis* isomer and the concentration of the asymmetric isomer was low ($<4\%$), but when the yield of ethylene-d_2 was low (Rh), *cis*- and *trans*-ethylene-d_2 were formed in about equal proportions and the concentration of the asymmetric isomer was considerable (10–15%).

The ethylene distributions have been interpreted in terms of a simple theoretical scheme. Two parameters s and p define the chances of adsorbed species acquiring deuterium (or hydrogen) atoms and of vinyl groups undergoing hydrogenation (or dehydrogenation). Each parameter is assigned a numerical value for each experiment by the interpolation procedure described. The chance of adsorbed species acquiring a deuterium atom rather than a hydrogen atom is shown to be high over each metal, but the chance of vinyl undergoing hydrogenation rather than dehydrogenation is high over Pt and Pd, low over Rh and intermediate over Ir. The manner in which each parameter varies with experimental conditions is discussed.

INTRODUCTION

In Parts I, II, and III of this series we have reported the kinetics and products obtained from the reaction of acetylene with hydrogen catalyzed by alumina-supported platinum (*1*), palladium (*2*), and rhodium and iridium (*3*). In this paper we report the reaction of acetylene with deuterium catalyzed by the same four metals, which was studied to obtain information on (i) the extent of isotopic exchange in the reactants and (ii) the distribution of deuterium in the ethylene produced. This use of an isotopic tracer provides information concerning the extent to which the adsorption of each reactant is reversible, and the interconvertibility or otherwise of adsorbed species.

Little work has been published on the reduction of the acetylenic triple bond by deuterium, which is surprising in view of the large number of investigations of olefin hydrogenation that have utilized deuterium as a tracer (*4*). In 1939 Farkas and Farkas

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(*5*), using a thermal conductivity technique, reported that the reaction took place on a platinum foil at 20° and that the rates of formation of deuterated acetylene and HD were negligible. In 1950 and 1952 Arnett and Crawford (*6*) and Douglas and Rabinovitch (*7*) used, respectively, palladium and nickel catalysts in the hope of preparing *cis*-ethylene-d_2. In both studies, all possible deuterated ethylenes were formed and were examined by mass and infrared spectrometry; the latter group of workers produced gas mixtures from reactions at —80° which contained 50% of the desired component. More recently, one of us (G. C. B.) used these spectrometric methods again to study the reaction between acetylene-d_2 and hydrogen catalyzed by nickel-pumice (*8*). In this work, a quantitative treatment of the distribution of deuterium in the ethylene was carried out.

The reduction of dimethylacetylene by deuterium using palladium-alumina has been reported by Meyer and Burwell (*9*) and Webb, Wells, and Phillipson have examined the same reaction using the other noble Group VIII metals supported on alumina (*10*).

Thus there have been no detailed studies of acetylene reduction by deuterium over the noble Group VIII metals carried out from the specifically catalytic point of view, and using modern spectrometric methods. In this paper and in Part V we shall present a detailed account of this reaction catalyzed by each of these six metals.

EXPERIMENTAL

The apparatus was exactly as described in Part I (*1*) except that the size of the reaction vessel was increased from 80 ml to 120 ml (for Rh, Pd, and Pt catalysts) or to 160 ml (for Ir).

Acetylene was purified as described previously (*1*). Deuterium gas was prepared by the electrolysis of 99.94% deuterium oxide which contained dissolved ignited sodium carbonate. The deuterium was purified by diffusion through a palladium thimble at 150°C. Material prepared in this way contained 99.5 atom % deuterium.

Preparation of the catalysts has been described (*3, 11*). Metal was supported on α-alumina at a concentration of 5% and samples weighed about 0.3 g.

Quantitative analysis for ethylene and ethane was carried out using the silver nitrate/benzyl cyanide/firebrick column described in Part I (*1*). This was only used at the beginning of the study to check that new catalyst samples used in this work were behaving as the previous samples (reported in Parts I–III) had done. Preparation of samples for mass spectrometric analysis was achieved as follows: The reaction mixture was pumped through a spiral trap cooled in liquid air, whereupon the hydrocarbons were quantitatively condensed out and the deuterium was pumped away. The hydrocarbon mixture was then separated into pure acetylene, ethylene, and ethane fractions using a chromatographic column of silica gel. The preparation of this column was as follows: 40 to 60 mesh B.D.H. silica gel was activated at 130°C for 3 hr, cooled in a vacuum desiccator, and then packed into a 46-inch spiral column. The column was operated at 20°C, using nitrogen as carrier gas: retention volumes were ethane, 66 ml; ethylene, 190 ml; and acetylene, 700 ml. Fractions were separately condensed into receivers on elution. C_4 hydrocarbons were retained by the column indefinitely.

Infrared analysis was used to determine the abundance of *trans-*, *asym-*, and *cis*-ethylene-d_2; the bands chosen were the ω_7 modes of each species which appear at 727 cm^{-1}, 752 cm^{-1}, and 843 cm^{-1}, respectively, according to the assignment of Arnett and Crawford (*6*). Spectra were obtained using a Unicam SP100. The gas cell had a capacity of 250 ml, a path length of 100 mm, and was fitted with potassium bromide plates. Pressures of ethylene from 3 to 15 mm were admitted and the cell was then filled to atmospheric pressure with dry air. Pure samples of the geometric isomers were not available, so calibration curves were constructed in the following manner. Spectra were obtained for a sample of deuteroethylene of known ethylene-d_2 content at pressures ranging from 2 to 17 mm. Percentage transmissions were measured for

TABLE 1
THE PLATINUM-CATALYZED REACTION
THE DEPENDENCE OF THE ETHYLENE COMPOSITION AND RELATED QUANTITIES UPON PRESSURE FALL, INITIAL REACTANT PRESSURES, AND TEMPERATURE

Temp. (°C)	$(P_{C_2H_2})_0$ (mm)	$(P_{D_2})_0$ (mm)	Pressure fall before analysis (mm)	Ethylene composition (%)					x	Ethylene-d_2 composition (%)			y	s	p	$(asym)_{calc}$
				$-d_0$	$-d_1$	$-d_2$	$-d_3$	$-d_4$		*cis*	*trans*	*asym*				
50	50	150	25	0.8	14.1	75.1	8.2	1.8	1.96	85	14	1	0.02	*0.91*	*0.76*	*1*
50	50	150	45	1.2	14.9	73.2	8.7	1.9	1.95	84	14	1	0.03	*0.90*	*0.75*	*1*
50	200	50	25	2.9	21.2	63.7	9.4	2.8	1.88	82	16	2	—	*0.85*	*0.67*	*3*
50	50	50	25	2.9	19.6	66.4	8.6	2.5	1.88	—	—	—	0.04	*0.86*	*0.70*	*2*
50	50	100	25	2.1	16.1	71.9	8.1	1.8	1.91	86	14	1	—	*0.89*	*0.75*	*2*
50	50	150	25	0.8	14.1	75.1	8.2	1.8	1.96	85	14	1	0.02	*0.91*	*0.76*	*1*
50	50	200	25	0.4	13.1	77.4	7.6	1.5	1.97	84	16	1	—	*0.92*	*0.79*	*1*
				0.6	*12.8*	*77.4*	*8.9*	*0.6*	*1.97*							
75	50	100	25	2.0	18.1	67.6	9.9	2.4	1.93	81	17	2	—	*0.88*	*0.69*	*2*
90	50	100	25	1.3	18.9	66.3	10.8	2.7	1.95	80	18	2	0.02	*0.88*	*0.66*	*3*
110	50	100	25	2.5	19.5	63.1	11.9	3.0	1.93	76	20	4	0.02	*0.86*	*0.63*	*4*
				1.7	*20.2*	*63.1*	*13.3*	*1.5*	*1.92*							

each isomer of ethylene-d_2 by regarding the bands of the *trans* and *asym* isomers as superimposed upon the fine structure of the *cis*-ethylene-d_2 band. The percentage transmissions were converted to isomer pressures by assuming that the extinction coefficients of the isomers were equal. This assumption, though not representing the rigorous truth, probably introduces but little error, since identical vibrational modes are being compared, and the ω_7 mode does not involve the stretching of C–H or C–D bands. On the basis of this assumption and a knowledge of the actual pressure of ethylene-d_2 in the sample, calibration graphs of the logarithm of the percentage transmission against the absolute pressure of each isomer of ethylene-d_2 were drawn. The percentage of each isomer present in a routine analysis was obtained by interpolation in the appropriate calibration graph. The pressure of total ethylene-d_2 calculated from a given spectrum agreed with the known pressure to within 10%.

Mass spectrometric analyses were carried out using a modified A.E.I. M.S.3 spectrometer. Acetylene and ethylene spectra were examined using an electron beam energy of 12.0 eV and three scans were made for each sample to ensure reliable average values of the ion currents. The ethylene distributions were calculated from the observed mass spectra in the usual way, assuming that carbon–hydrogen and carbon–deuterium bonds had the same chance of fission during the fragmentation process. Pure ethylene-d_0 gave ions at mass numbers 29, 28, 27, and 26 attributable to $C^{13}CH_4^+$, $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$, the intensities of the third and fourth ions being, respectively, 1.6% and 4.8% of that of the parent ion. Pure acetylene-d_0 gave ions at masses 27 and 26 only, i.e., no fragmentation occurred. Correction for C^{13} was made in the usual way.

The isotopic purity of deuterium samples was determined using an ionizing voltage of 60 eV. Ethane, ethylene, and acetylene gave no ions of $m/e = 2$, 3, or 4; thus the isotopic purity of deuterium was determined using gas mixtures extracted directly from the reaction vessel.

RESULTS

The examination of each metal followed a similar pattern, and the results are shown in Tables 1 (Pt), 2 (Pd), 3 (Ir), and 4 (Rh). The left-hand sections of these tables give the experimental conditions; the abbreviation $(P_X)_0$ denotes the initial pressure of reactant X ($= C_2H_2$ or D_2). The center sections give

(i) the ethylene distributions, where ethylene-d_i is $C_2H_{4-i}D_i$ for which $0 \leqslant i \leqslant 4$;

(ii) x, the deuterium number of the ethylene, which is defined as the mean value of i for the ethylene sample, i.e., $x = \Sigma i(-d_i)/100$,

(iii) the isomeric composition of the ethylene-d_2;

(iv) y, the hydrogen number of the residual "deuterium" which had the composition H_yD_{2-y}.

The right-hand sections of these tables provide values of two parameters, s and p, and the calculated value of the percentage of ethylene-d_2 in the asymmetric form, $(asym)_{calc}$. These quantities are derived from the treatment presented in Part II of the Discussion, but are included here for convenience.

Typical calculated ethylene distributions, together with the values of s and p used in their derivation, are contained in the Tables and are shown in italics.

The Dependence of the Ethylene Distribution on Experimental Variables

When products were analyzed after 25 and 50 mm pressure fall (Rh, Pd, Pt) or 12 and 25 mm (Ir) the ethylene distributions were similar, the yield of ethylene-d_2 having fallen by only 2% or so. Consequently, extraction after 25 mm pressure fall was adopted as standard procedure when other experimental parameters were being varied.

As the initial deuterium pressure was increased, so the yield of ethylene-d_2 and x increased, whichever metal was used. Sensitivity of the distribution to this variable

TABLE 2
THE PALLADIUM-CATALYZED REACTION

Temp. (°C)	$(P_{C_2H_2})_0$ (mm)	$(P_{D_2})_0$ (mm)	Pressure fall before analysis (mm)	Ethylene composition (%)					x	Ethylene-d_2 composition (%)			y	s	p	$(asym)_{calc}$
				$-d_0$	$-d_1$	$-d_2$	$-d_3$	$-d_4$		*cis*	*trans*	*asym*				
26	50	50	50	4.5	26.0	58.0	9.7	1.8	1.78	79	18	3	0.00	*0.82*	*0.70*	*3*
26	200	50	25	4.8	27.3	56.9	9.6	1.4	1.76	81	16	3	0.00	*0.79*	*0.66*	*4*
26	50	50	25	3.5	25.2	60.9	9.1	1.3	1.79	82	16	2	0.00	*0.82*	*0.70*	*3*
26	50	100	25	3.6	22.7	65.4	7.2	1.1	1.80	82	16	2	0.00	*0.84*	*0.75*	*3*
26	50	200	25	3.4	21.7	66.7	7.0	1.2	1.81	83	15	2	0.01	*0.87*	*0.76*	*2*
26	50	250	25	2.5	20.4	69.9	6.2	1.0	1.83	85	14	1	0.01	*0.87*	*0.80*	*1*
0	50	100	25	2.4	20.3	68.1	7.9	1.3	1.86	84	14	2	0.00	*0.86*	*0.75*	*2*
15	50	100	25	2.3	22.0	65.2	8.8	1.7	1.86	83	15	2	0.00	*0.85*	*0.71*	*3*
				1.9	*22.0*	*65.2*	*10.0*	*0.8*	*1.86*							
36	50	100	25	3.8	24.8	59.8	10.0	1.6	1.81	80	17	3	0.00	*0.81*	*0.66*	*4*
46	50	100	25	4.0	26.2	56.5	10.9	2.4	1.81	78	19	3	0.00	*0.80*	*0.62*	*5*
				3.4	*26.5*	*56.5*	*11.7*	*1.2*	*1.79*							

TABLE 3
The Iridium-Catalyzed Reaction

Temp. (°C)	$(P_{C_2H_4})_0$ (mm)	$(P_{D_2})_0$ (mm)	Pressure fall before analysis (mm)	Ethylene composition (%)					x	Ethylene-d_2 composition (%)			y	s	p	$(asym)_{calc}$
				$-d_0$	$-d_1$	$-d_2$	$-d_3$	$-d_4$		*cis*	*trans*	*asym*				
42	50	100	12	1.6	12.6	52.8	23.2	9.8	2.27	72	25	3	0.06	*0.88*	*0.39*	*6*
42	200	50	25	3.6	19.5	50.7	18.3	7.9	2.08	75	20	5	—	*0.81*	*0.39*	*9*
42	50	50	25	3.0	19.4	48.9	19.5	9.2	2.13	73	22	5	0.23	*0.81*	*0.36*	*10*
42	50	100	25	2.1	15.8	49.9	21.9	10.3	2.22	72	24	4	—	*0.84*	*0.35*	*9*
42	50	145	25	2.3	15.3	51.3	21.8	9.3	2.20	—	—	—	—	*0.85*	*0.38*	*8*
42	50	200	25	1.8	15.2	51.2	22.5	9.3	2.23	73	22	5	0.05	*0.86*	*0.37*	*7*
				1.3	*14.6*	*51.2*	*25.4*	*7.8*	*2.24*							
30	50	100	25	1.7	13.8	53.5	21.9	9.1	2.23	77	21	2	0.12	*0.88*	*0.40*	*6*
65	50	100	25	1.1	16.3	46.4	23.7	12.5	2.30	69	27	4	—	*0.84*	*0.30*	*10*
100	50	100	25	2.2	15.2	40.9	26.1	15.6	2.38	62	31	7	—	*0.82*	*0.24*	*13*
				1.4	*15.0*	*40.9*	*29.6*	*12.8*	*2.37*							
120	50	100	25	1.9	13.3	38.3	27.0	19.5	2.49	63	30	7	0.16	*0.78*	*0.19*	*16*

TABLE 4
The Rhodium-Catalyzed Reaction

Temp. (°C)	$(P_{D_2})_0$[a] (mm)	Pressure fall before analysis (mm)	Ethylene composition (%)					x	Ethylene-d_2 composition (%)			y	s	p	$(asym)_{calc}$
			$-d_0$	$-d_1$	$-d_2$	$-d_3$	$-d_4$		*cis*	*trans*	*asym*				
134	110	50	1.9	13.7	35.4	28.6	20.4	2.52	46	41	13	0.19	*0.80*	*0.15*	*8*
134	50	25	2.7	15.0	33.5	27.8	21.0	2.50	45	41	14	0.23	*0.75*	*0.11*	*22*
134	110	25	1.2	11.7	36.7	27.7	22.7	2.59	48	40	12	0.11	*0.82*	*0.18*	*14*
			1.0	*11.2*	*36.7*	*32.5*	*18.9*	*2.58*							
134	150	25	1.3	10.1	35.7	30.0	22.9	2.63	51	39	10	0.07	*0.85*	*0.17*	*13*
134	205	25	0.5	8.9	37.8	29.2	23.6	2.67	51	38	11	0.05	*0.88*	*0.21*	*9*
156	110	25	0.6	10.1	34.4	29.4	25.5	2.69	46	42	12	0.12	*0.86*	*0.16*	*14*
177	110	25	0.2	9.0	31.3	30.3	29.2	2.79	41	46	13	0.24	*0.87*	*0.14*	*13*
			0.6	*7.5*	*31.3*	*34.3*	*26.3*	*2.78*							
200	110	25	1.6	8.4	29.2	29.9	30.9	2.80	38	48	14	0.26	*0.84*	*0.11*	*12*

[a] $(P_{C_2H_2})_0 = 50$ mm throughout.

decreased in the sequence, Pt $>$ Pd $>$ Rh $>$ Ir. Over Pt and Pd this increase in ethylene-d_2 was accompanied by a reduction in the yields of all other isotopic isomers, whereas over Rh and Ir the yields of ethylene-d_2, -d_3, and -d_4 (Rh only) were all favored by increasing deuterium pressure.

The yield of ethylene-d_2 was diminished slightly when initial acetylene pressure was increased from 50 to 200 mm using Pt and Pd, and it was enhanced a little by the same treatment using Ir. Rh was not studied in this connection.

An increase in temperature reduced the yields of ethylene-d_2 and favored all other isotopic isomers, except ethylene-d_1, when using Rh and Ir. Pd provided the most temperature sensitive distributions and Rh and Pt the least sensitive. The deuterium number of the ethylene was fairly independent of temperature when Pt and Pd were used, but it increased with increasing temperature when Rh and Ir were used. Ethylene-d_2, -d_3, and -d_4 were produced in similar concentrations over Rh at 177° and 200°C. Neither C_2HD nor C_2D_2 was produced in the gas phase in any experiment.

DISCUSSION

I. *General*

The absence of acetylene exchange means either that no deuterated acetylenes were formed on the catalyst surface or that they were formed but that their rate of desorption was negligible. The theoretical treatment given below indicates that both acetylene-d_1 and -d_2 were indeed formed, and so the second alternative given above is most probably valid. Negligible acetylene desorption is consistent with the very strong adsorption of acetylene which was recorded in Parts I–III (*1–3*).

The extent to which the hydrogen exchange reaction occurred, giving HD and H_2 in the gas phase, varied from metal to metal in the sequence

$$\mathrm{Rh} \geq \mathrm{Ir} \gg \mathrm{Pt} > \mathrm{Pd} \qquad (1)$$

Over rhodium and iridium the rate of hydrogen atom recombination was similar to the rate of hydrogenation, whereas, at the other extreme, hydrogen desorption from palladium was negligible. The above sequence was also observed in our studies of the reaction of ethylene with deuterium using the same catalyst preparations (*11*). As expected, the actual rates of hydrogen exchange were much slower during acetylene hydrogenation than when ethylene was hydrogenated, because the steady state concentration of adsorbed hydrogen is smaller in the former reaction, acetylene being more strongly adsorbed than ethylene on all four metals (*1–3*).

The Distributions of Deuterium in the Ethylene

Each metal produced all possible deuterated ethylenes. Hereafter, we shall refer to the yields of isotopic ethylenes taken collectively as the "ethylene distribution." The maximum in the distributions was always at ethylene-d_2, except over rhodium at 177° and 200°C, and the yields of ethylene-d_2 varied in the sequence

$$\mathrm{Pt} > \mathrm{Pd} > \mathrm{Ir} > \mathrm{Rh} \qquad (2)$$

Pt at 50° gave as much as 77% ethylene-d_2. Since the simplest conceivable mechanism for ethylene formation involves the simultaneous *cis* addition of two deuterium atoms to acetylene to give solely *cis*-ethylene-d_2 (*4*), we see immediately that the complexity of the reaction varies as the *reverse* of sequence (2), but that even over Pt the mechanism does not approximate to the simplest model.

The isomeric composition of the ethylene-d_2 is related to the fraction that it constituted of the total ethylene yield. Thus, when its yield was high, as over Pt and Pd, its major component was the *cis* isomer and the yield of the *asym* isomer was very low ($<4\%$), but when its yield was low, as over Rh, the *cis*-, and *trans*-ethylene-d_2 were formed in about equal proportions and the yield of *asym*-ethylene-d_2 was comparatively high (10–15%). Most surprisingly, a plot of the yields of *cis*- and *asym*-ethylene-d_2 (expressed as a percentage of the total ethylene-d_2) versus the yield of ethylene-d_2 (expressed as a per-

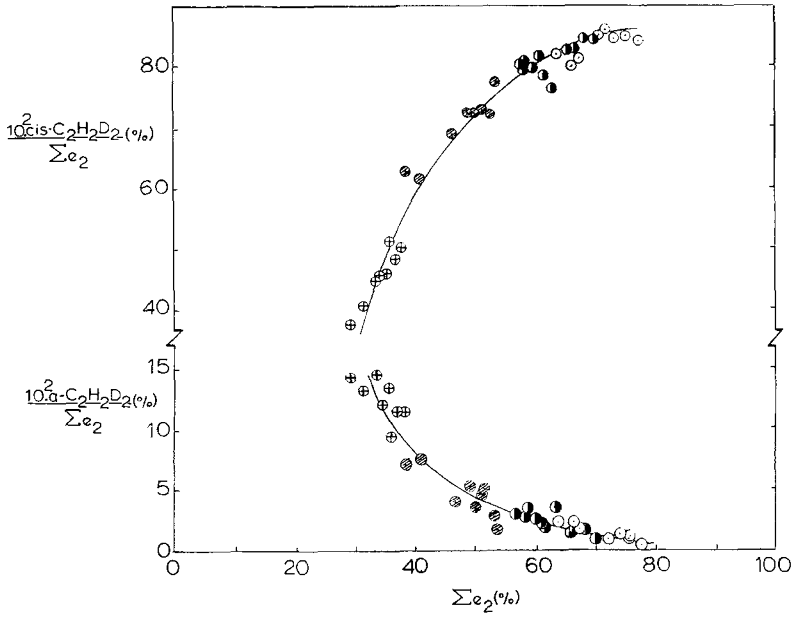


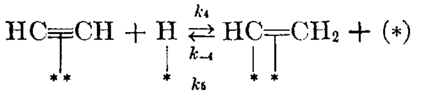
FIG. 1. The variation of the yields of *cis*- and *asym*-ethylene-d_2 (expressed as a percentage of the total ethylene-d_2) with the total ethylene-d_2.

centage of the total ethylene) gives a pair of smooth curves on which the points for *all four* metals lie (Fig. 1). This strongly suggests that the four metals catalyze acetylene hydrogenation by a fundamentally similar mechanism, and that a gradual variation of some feature of the mechanism is responsible for the apparent diversity of ethylene distributions provided by the four metals.

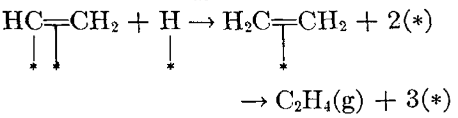
Since acetylene exchange did not occur, the deuterium number of the ethylene (x in the Tables) should vary from metal to metal as in sequence (1), because the appearance of hydrogen in the gas phase should be compensated by the introduction of more than two deuterium atoms (on average) into the ethylene. The observed sequence is indeed sequence (1) but x for palladium is substantially less than the expected value of 2.00. This was caused by a complex effect of C_4 hydrocarbon formation, which accompanies the production of ethylene and ethane (*1–3*). For reasons which we do not understand, the deuterium content of the C_4 hydrocarbons was higher than expected and this excess was related to the deficiency of deuterium in the ethylene. Less acetylene was converted to C_4 hydrocarbons over platinum where x was only slightly less than 2.00; over rhodium and iridium any polymer-forming effect was masked by the high x due to rapid hydrogen exchange.

II. *Quantitative Treatment of Ethylene Distributions*

We now attempt to interpret quantitatively the ethylene distributions quoted in this paper. First, we must decide the number of adsorbed species that are involved. Clearly, all intermediates that participate in the direct ethylene-forming process are relevant; these are adsorbed acetylene, adsorbed vinyl, and adsorbed ethylene. The direct ethylene-forming steps are (*1–3*)

 (4)

$$\underset{**}{HC{\equiv}CH} + \underset{*}{H} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \underset{*\ *}{HC{=}CH_2} + (*) \qquad (4)$$

 (5)

$$\underset{*\ *}{HC{=}CH_2} + \underset{*}{H} \xrightarrow{k_6} \underset{*}{H_2C{=}CH_2} + 2(*) \rightarrow C_2H_4(g) + 3(*) \qquad (5)$$

(The equation numbers are those used in previous papers.) However, we must also consider whether adsorbed ethyl is a relevant intermediate, i.e., whether the ethane-forming process influences the ethylene distribution via the alkyl reversal reaction: $C_2X_4(ads) + X(ads) \rightleftharpoons C_2X_5(ads)$ where $X = H$ or D. Our studies of the ethylene–deuterium reaction have shown that ethylene exchange occurs efficiently by the alkyl reversal process on Rh and Pd, but relatively inefficiently on Ir and Pt below 100°C (*11*). However, acetylene is more strongly adsorbed than ethylene, and thus the surface coverage of ethylene during acetylene hydrogenation is expected to be smaller, than during ethylene hydrogenation by one or two orders of magnitude. Consequently, we have assumed that ethylene exchange by the alkyl reversal process is negligible over Pt and Ir, and of very minor importance over Rh and Pd. This conclusion receives support from two sources. First, studies of but-2-yne hydrogenation over the noble Group VIII metals have shown that virtually all butene is produced by the direct hydrogenation of the alkyne and that the contribution of alkyl reversal is negligible (*9, 10*). Secondly, there is no correlation between the selectivity that these metals show for ethylene formation [$Pd > Pt \geqslant Rh > Ir$] (*1–3*), and their specificity for ethylene-d_2 formation [$Pt > Pd > Ir > Rh$]. A correlation would have been observed had the major product of steps (4) and (5) been adsorbed *cis*-ethylene-d_2, and had the observed ethylene distributions been formed by the subsequent formation and decomposition of adsorbed ethyl.

Consequently, in the treatment below, the ethylene distributions will be interpreted in terms of the mechanism shown in steps (4) and (5) above. The treatment used is a modification of that described in ref. (*8*).

Our notation is as follows: The symbols a_i and e_i denote, respectively, adsorbed acetylenes and ethylenes containing i deuterium atoms. Since *sym*- and *asym*-ethylene-d_2 are distinguishable species we differentiate between them by adding a second suffix, so that they are denoted by e_{21} and e_{22}, respectively.

We suppose that, in the steady state, acetylene-d_0, -d_1, and -d_2 are formed in concentrations a_0, a_1, and a_2, respectively. These acetylenes each have the same chance s of gaining a deuterium atom and the same chance $(1 - s)$ of gaining a hydrogen atom, the origin of these atoms being unspecified. In this way, the six possible vinyls are formed. Each vinyl has the same chance p of undergoing hydrogenation to ethylene or the chance $(1 - p)$ of loosing a hydrogen or deuterium atom and reverting to adsorbed acetylene. In the conversion of vinyl to ethylene the chance of gaining a deuterium atom is again s and of gaining a hydrogen atom is $(1 - s)$.

No distinction was made between vinyls having structures (I) and (III) because their interconversion is envisaged via the free radical form (II) (see Fig. 2). This free radical species is responsible for acetylene polymerization (*1–3, 8, 12*) and we also consider it to be a transitory intermediate between the normal vinyl group and adsorbed acetylene which is formed by loss of a hydrogen atom (*10a*).

The quantitative treatment described in ref. (*8*) utilized an approximate algebraic relationship between a_0, a_1, and a_2. Kemball has pointed out to us (*13*) that a rigorous steady state treatment is sufficiently straightforward to render these approximations unnecessary, and in the present work the following equations resulting from his steady state treatment have been employed:

$$a_2[1 - 0.5(1 + s)(1 - p)] = 0.25a_1(1 - p)$$

$$0.5a_0s(1 - p) = a_1\left\{0.25(1 - s)(1 - p) + p\left[\frac{1 - 0.5(1 + 0.5s)(1 - p)}{1 - 0.5(1 + s)(1 - p)}\right]\right\}$$

The ethylene distribution, $e_0 \ldots e_4$, is then obtained by multiplying a_i by the appropriate chances that the events described above will occur. In this scheme e_{21} and e_{22} are distinguishable species, and so the percentage of ethylene-d_2 in the asymmetric form is simply calculated as, $10^2e_{21}/(e_{21} + e_{22})$ and can be compared with the experimentally determined percentage, as has been done in the Tables.

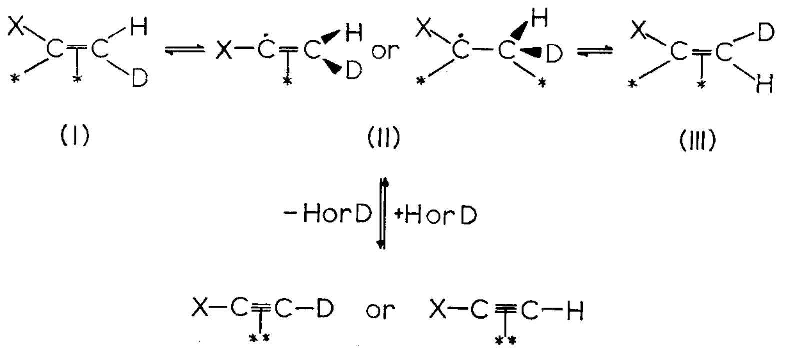


FIG. 2. The interconversion of isotopically distinguishable vinyls and the suggested mode of their dehydrogenation to acetylene [X = H or D].

Ethylene distributions calculated in this way are of little value in themselves because s and p cannot be chosen from an inspection of an experimental distribution. The following procedure was therefore adopted. Results from 30 such calculations enabled a graph to be constructed which relates Σe_2 $(= e_{21} + e_{22})$, s, p, and deuterium number, x. First, it was necessary to define a function R, such that $R = (1-s)\ (1-p)$. Calculations were carried out for various values of R using values of p between 0.1 and 0.8; the results were then plotted as shown in Fig. 3. The figure shows two series of curves; the transverse curves give the dependence of Σe_2 upon R at constant p, and the second series of curves gives the dependence of Σe_2 upon R at constant deu-

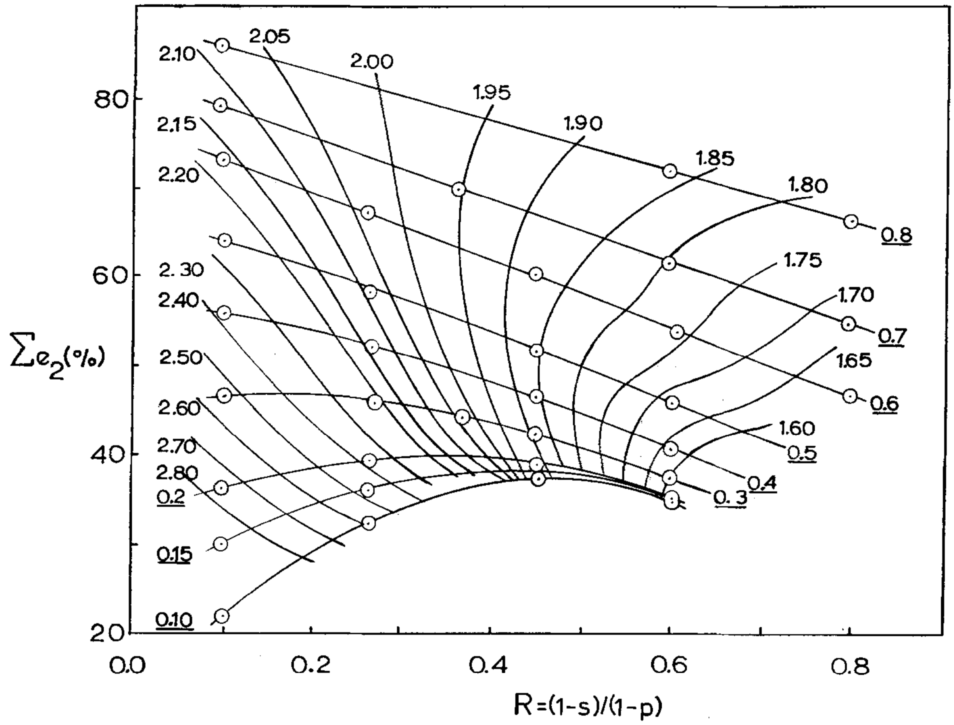


FIG. 3. Theoretical interrelationships between Σe_2, R, p, and deuterium number. Numbers on the graph which range from 0.10 to 0.80 are values of p and refer to the transverse series of curves; numbers which range from 1.60 to 2.80 are deuterium numbers and refer to the other series of curves.

terium number (x). [Figure 3 differs from the corresponding figure in ref. (*8*); this is a measure of the difference between the former approximate treatment and the present rigorous treatment.] Graphs of e_i versus R for the various values of p were also constructed.

Theoretical distributions for any combination of s and p were obtained by a method of interpolation. The experimental values of Σe_2 and x were used to obtain the relevant value of R from Fig. 3. The ethylene distribution was then obtained from graphs of e_i versus R, using the appropriate value of p. The tables show typical comparisons between observed and calculated distributions, the latter being shown in italics underneath the experimental distributions with which they should be compared. The condition $\Sigma e_i = 100.0$ has *not* been imposed, and it will be noted that $\Sigma e_i = 100.0 \pm 0.5$ or better.

The agreement between observed and calculated distributions is satisfactory. For each metal the calculated values for ethylene-d_3 exceeded those observed, whereas the observed ethylene-d_4 exceeded the calculated values, but the disparities are not serious. Calculated and observed ethylene-d_0 and -d_1 and x agree well in most cases. The calculated values of $(asym)_c$ slightly exceed the observed values, but generally the agreement is most gratifying.

This scheme predicts an interdependence of $(asym)_c$ and Σe_2 if R is constant; the predicted curve is convex with respect to the origin and $(asym)_c$ tends to zero as Σe_2 approaches 100%. The experimental curve has this predicted shape (see Fig. 1) but R is not constant from one experiment to another, and differs considerably between one metal and another, and thus the curve shows some scatter.

The Values of s and p and their Dependence upon Experimental Variables

The values of s and p derived from the above scheme for each experiment are recorded in the Tables. Values of s vary from 0.75 to 0.95, taking all four metals together, which shows that the chance of adsorbed species acquiring deuterium was high under all conditions. Over Pd and Pt p ranged from 0.80 to 0.95, i.e., the chance of vinyl undergoing hydrogenation to ethylene was 4 to 19 times greater than the chance of its dehydrogenation to acetylene. Consequently, the concentrations of adsorbed acetylene-d_1 and -d_2 were small (commonly about 13% and 1% of the acetylene-d_0 concentration, respectively) and this resulted in the yields of ethylene-d_3 and -d_4 being considerably smaller than ethylene-d_2. The situation at the Rh and Ir surfaces was quite different; here p varied from 0.04 to 0.21 (Rh) and from 0.28 to 0.39 (Ir) showing that the majority of vinyls dehydrogenated to acetylenes. Consequently, concentrations of acetylene-d_1 and -d_2 were high. For example, when $R = 0.263$ and $p = 0.15$ (a typical case for Rh), the composition of the adsorbed acetylene was $C_2H_2 = 35\%$, $C_2HD = 39\%$, and $C_2D_2 = 26\%$; or, when $R = 0.266$ and $p = 0.4$ (a typical case for Ir) the composition was $C_2H_2 = 63\%$, $C_2HD = 29\%$, and $C_2D_2 = 8\%$. These values of a_1 and a_2, and the high value of s combined to produce much higher yields of ethylene-d_3 and -d_4 than were observed over Pd and Pt. Since the metal surface is mainly covered with acetylene in these reactions (*1–3*), the concentrations of deuterated acetylenes were sufficient to produce measurable exchange reactions had adsorption been reversible.

The similarity of s over all four metals requires comment in view of the wide variations of p. The tables show that virtually no hydrogen exchange occurred over Pd and Pt and consequently hydrogen atoms expelled from vinyls remained adsorbed and were eventually acquired by other acetylenes or vinyls. In this situation high values of both s and p are mutually consistent. However, considerable hydrogen exchange occurred over Rh and Ir, and in this case hydrogen atoms expelled from vinyls were partially replaced by deuterium; thus a high value of s is attained in spite of p being low.

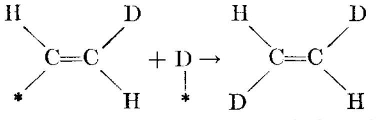
When the initial deuterium pressure was increased, s increased over all four metals and p increased over Rh, Pd, Pt but not over Ir (see Tables 1–4). An increase in p is expected because $\theta_D \propto P_{D_2}{}^n$ [where n is positive (*1–3*)] and the rate of vinyl hydrogenation is proportional to θ_D whereas its dehydrogenation is not. The parameter s increases because the larger the surface coverage of deuterium becomes the greater is the chance of adsorbed species acquiring deuterium; s will also increase as a result of the increase in p since the release of hydrogen atoms onto the surface is reduced.

An increase in acetylene pressure reduced the surface coverage of hydrogen and deuterium atoms (*1–3*). The reasoning of the previous paragraph would predict a decrease in p and s. This is observed for Pd and Pt; over Ir s remained constant and p increased, for which there is no ready explanation. Rhodium was not studied in this connection.

The effect of temperature variation, using Ir, Pd, and Pt, was caused (according to the decreasing values of s and p given by the scheme) by an increase in the rate of interconversion of acetylenes and vinyls. This provides another similarity between this study and the ethylene–deuterium reaction (*11*), where we have shown that the analogous ethylene–ethyl interconversion is favored by an increase in temperature. For acetylene deuteration over Rh (Table 4), the variations of s and p with temperature are small and appear to pass through a shallow maximum at about 160°. We could conclude that, below 160°, the surface coverage of deuterium and hydrogen increases with increasing temperature and that this is more important than the increase in the rate of interconversion of acetylenes and vinyls.

The Isomeric Composition of Ethylene-d_2

It was pointed out in Part I of this Discussion that the fraction of ethylene-d_2 appearing as the *cis* isomer is high when the fraction which the ethylene-d_2 forms of the total ethylene is high; the reverse is also true (see Fig. 1). The reason is now clear. Whenever experimental conditions are changed so that the yield of ethylene-d_2 is decreased, this occurs because the number of acetylene–vinyl interconversions undergone by a given hydrocarbon unit has been increased. Now, each sequence vinyl–acetylene–vinyl makes possible the exchange of hydrogen atoms originally associated with the acetylene, and this is the essential step for the formation of *trans*- and *asym*-ethylene-d_2. *trans*-Ethylene-d_2, for example is formed by the reaction of (III) (see Fig. 2) with a deuterium atom.



(III) *trans*-ethylene-d_2

Thus, the lower p, the more important is the acetylene–vinyl interconversion and the higher the yields of *trans*- and *asym*-ethylene-d_2 should be. This is in complete accord with the experimental results.

The free radical form of adsorbed vinyl has played an important role in this discussion. Further studies, especially of the mechanism of acetylene polymerization, are required to furnish further information about this adsorbed species.

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