

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1963, by the American Chemical Society

VOLUME 85, NUMBER 19

OCTOBER 5, 1963

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

The Reaction between Deuterium and Dialkylacetylenes on Palladium Catalysts

BY EDWIN F. MEYER¹ AND ROBERT L. BURWELL, JR.

RECEIVED MAY 16, 1963

At 14°, 2-butyne and deuterium react on a 0.03% palladium-on-alumina catalyst to form *cis*-2-butene-2,3-*d*₂ almost exclusively as long as unreacted 2-butyne remains. The yield in multiply exchanged *cis*-2-butene, the other butenes, and butane sums to but 1%. The proportion of the by-products increases with temperature and reaches about 6% at 58°. In reaction with a mixture of hydrogen and deuterium, the hydrogen-deuterium exchange reaction is almost completely inhibited. The distribution of *cis*-2-butene-*d*₀, -*d*₁, and -*d*₂ is random but there is an incorporation isotope effect of 1.6 favoring hydrogen. Thus, hydrogen is adsorbed dissociatively and the surface hydrogen atoms are scrambled before addition to 2-butyne, the rate of desorption of hydrogen is negligible, and, in competition, hydrogen adsorbs preferably by a factor of 1.6. The reaction of deuterium with 3-hexyne in the liquid phase on a 13.8% palladium-on-alumina catalyst gives similar results except that the proportion of by-products is several times larger. The mechanism of the reaction appears to be the same in both phases and the somewhat lower selectivity may result from the much lowered hydrogen concentration in the liquid phase.

A substantial fraction of the investigations relating to the mechanism of heterogeneous catalysis has dealt with the interactions of hydrocarbons and hydrogen. The aim of most of these investigations has been the identification of the surface intermediates involved in these reactions. Studies employing deuterium as an isotopic tracer coupled with variation of hydrocarbon structure and with reactions with stereochemical consequences have been particularly revealing. Although much has been learned, our understanding of possible surface intermediates in hydrocarbon reactions is incomplete. Most previous studies have involved isotopic exchange reactions of alkanes or reactions of olefins. Few studies have involved multiply unsaturated species. Yet intermediates involved in such reactions are important to any general understanding. In this paper, we report a study of the reaction between deuterium and 2-butyne in the vapor phase on palladium-on-alumina and between deuterium and 3-hexyne in the liquid phase on palladium-on-alumina. In the following paper we report the reaction between deuterium and 1-butyne, 1,2-butadiene, and 1,3-butadiene in the vapor phase.

The hydrogenation of a disubstituted acetylene on palladium catalysts has been a standard method for the preparation of *cis*-olefins for many years.² Almost all studies of this reaction have involved liquid phase reactions and few were aimed at mechanism. A few years ago we reported a study of the reaction between hydrogen and 2-butyne on palladium-on-alumina in the vapor phase.³ The reaction was almost entirely selective, that is, almost no alkane was formed initially and the alkene product did not react further as long as unreacted butyne was present. Once all butyne had disappeared, the alkene underwent both hydrogenation

and isomerization. Further, the reaction was highly stereoselective, that is, the olefinic product was almost entirely *cis*-2-butene. Trace amounts of the other butenes and of butane were observed but these seemed to accompany the original formation of 2-butene and not to be the products of its subsequent reaction. Even at $H = 0.98$ (H represents the number of moles of hydrogen added per mole of acetylene), the small amount of residual 2-butyne completely poisoned subsequent reaction of *cis*-2-butene.

We may say that this vapor phase reaction was about 99% selective and stereoselective. From previous reports,² liquid phase reactions on unpoisoned palladium catalysts are apt to be about 90% selective and 90% stereoselective.

Since the vapor phase reaction seemed to be a very simple one, it seemed desirable to study the reaction further by use of deuterium and to study an analogous reaction in the liquid phase. 2-Butyne being too low boiling (b.p. 28°), 3-hexyne (b.p. 80°) was employed in the latter reaction. There are very few comparable data on catalytic reactions proceeding both in the liquid and in the vapor phase. Thus we hoped that the interest of this study might extend beyond that of the reactions actually studied.

Experimental

Materials.—Palladium dichloride was dissolved in water containing the minimum necessary hydrochloric acid and the resulting solution was used to impregnate 40 to 100 mesh Houdry hard alumina, grade 100. The ratio of palladium chloride to alumina was chosen to give a 0.03 wt. % palladium-on-alumina catalyst. Since the yellow color in the solution disappeared rapidly upon the addition of alumina, it is probable that the palladium was largely adsorbed on the outer portion of the alumina pellets. The solution plus alumina was heated at 75° for 3 hr. and then evaporated to dryness on a steam bath. The catalyst was reduced at 160° in a stream of hydrogen and separated into fractions of which the 40–60 mesh material was used in this research. The 13.8% palladium-on-alumina catalyst had been prepared by Dr. B. K. C. Shim.⁴

(4) R. L. Burwell, Jr., B. K. C. Shim, and H. C. Rowlinson, *J. Am. Chem. Soc.*, **79**, 5142 (1957).

(1) Further details are available in the Ph.D. thesis of E. F. Meyer, Northwestern University, 1963.

(2) For a review of the descriptive chemistry of this reaction, see R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

(3) W. M. Hamilton and R. L. Burwell, Jr., "Actes du Deuxième Congrès International de Catalyse," Éditions Technip, Paris, 1961, p. 987.

Deuterium was obtained from General Dynamics Corporation. The 2-butyne obtained from Farchand Research Laboratories was rather impure and was fractionally distilled and collected in a vessel to be directly sealed to the reaction apparatus. By gas chromatography the final purity was better than 99.9%. The 3-hexyne as purchased (Farchand Research Laboratories) was about 74% 3-hexyne. It was redistilled to a purity of better than 99%.

Apparatus.—A flow reactor was employed for vapor phase studies. Since the heat of hydrogenation of 2-butyne is large, the glass walls of the catalyst chamber which was in the form of a U-tube were thinned by treatment with hydrofluoric acid. The catalyst was also diluted with about ten times its weight of 40–60 mesh glass beads. The catalyst chamber was immersed in a water thermostat.

The hydrogen and deuterium streams were each purified by passage over nickel-kieselguhr at 400°, Drierite, Linde Molecular Sieve 5A, and nickel-kieselguhr at room temperature.

2-Butyne was fed as a liquid from a motor-driven 10-cc. syringe to the top of a tube at the bottom of which deuterium was introduced. Deuterium flow rates were measured by a bubble meter at the outlet of the apparatus. Glass-Teflon needle valves were employed to isolate the syringe and to separate the butyne storage bulb from the syringe. Analytical samples of reaction products were obtained either by insertion of a gas syringe through a serum cap located just beyond the catalyst chamber or, where individual compounds were to be isolated by gas chromatography, a 50-cc. tube with a stopcock at one end was placed in the line following the catalyst chamber. After a suitable period on line, the tube was removed and capped at the open end with a serum cap.

Before use, the catalyst was treated overnight at 370° in a stream of hydrogen. When deuterium was to be used, the hydrogen stream was replaced by one of deuterium for 15 min. The furnace was then replaced by the water bath, the hydrogen or deuterium flow rate was established at about 43 mmoles per hr., and the butyne feed rate was started at 21.8 mmoles per hr.

The liquid phase reactions employed a miniature batch reactor previously described.⁵ About 1.5 cc. of 3-hexyne and 10 mg. of 13.8% palladium-on-alumina were employed. The apparatus involves recycle of deuterium gas through a porous disk into the suspension of hydrocarbon and catalyst.

Analysis.—The analysis of the 2-butyne system was performed gas chromatographically on a tricresyl phosphate column. The 3-hexyne system was first separated into 3-hexyne and products on a Castorwax column. The latter fraction was then analyzed on a silver nitrate-triethylene glycol column. In a number of instances, the product mixtures were separated into the individual components and these were analyzed separately by mass spectroscopy on a Consolidated Electrodynamic Corp. Model 21-130 instrument which had been provided this department by matching funds from the National Science Foundation. The ionizing voltages were adjusted to give the minimum yields of species lying just below the parent peak while at the same time giving adequate sensitivity. In one case, a series of successive isolations of *cis*-2-butene from the product of reaction of 2-butyne with deuterium gave enough material for nuclear magnetic resonance spectroscopy at 60 Mc.

Results

Vapor Phase.—The addition of deuterium to 2-butyne exhibits essentially the same selectivity and stereoselectivity as that reported for hydrogen.³ A number of runs was made and analyzed mass spectrographically. Those for which *H* (moles of deuterium added per mole of butyne) was less than unity are reported in this paper. In all cases the unreacted 2-butyne was devoid

TABLE I
ADDITION OF DEUTERIUM TO 2-BUTYNE

Run	Temp., °C.	Wt. cat., g.	Hydrocarbon fraction				
			2-yne	<i>cis</i> -2	<i>trans</i> -2	1-Butene	Butane
63c	14	0.321	0.220	0.772	0.007	0.000	0.001
32b	27	.171	.529	.460	.004	.002	.005
35b	58	.194	.141	.824	.012	.007	.016
Isotopic distribution of <i>cis</i> -2-butene							
			<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> _{av} ^a
63c	14		0.005	0.018	0.975	0.002	1.97
32b	27		.002	.058	.937	.003	1.94
35b	58		.010	.054	.914	.022	1.95

^a Average number of deuterium atoms per molecule of *cis*-2-butene.

(5) G. V. Smith and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **84**, 925 (1962).

of deuterium. No isomerization product of 2-butyne could be detected. Results for three runs are given in Table I. At 30°, the product consists of about 97.5% *cis*-2-butene, 1% *trans*-2-butene, 1% butane, and 0.5% of 1-butene.

Three runs were made at 15° in which an approximately equimolar mixture of deuterium and hydrogen was employed instead of deuterium. Concordant results were obtained. When the mixture of hydrogen and deuterium without the 2-butyne was passed over the catalyst at the conventional flow rate the following results were obtained

	H ₂ , %	HD, %	D ₂ , %
Before	50.2	1.0	48.8
After	27.2	45.8	27.0
Equil.	26.3	47.4	26.3

The isotopic exchange reaction went nearly to equilibrium.

In run 53, 0.32 g. of catalyst, H₂/D₂ = 1.065, and with the usual ratio of total hydrogen to butyne, the HD content of the hydrogen increased from 1 to 4%. The exchange reaction is highly inhibited by the presence of 2-butyne. In the absence of 2-butyne, the exchange reaction had proceeded to at least 4 half-lives. Thus, the presence of 2-butyne decreases the reaction, H₂ + D₂ = 2HD, by a factor of 40 or greater.

The product of run 53 consisted of 39.2% *cis*-, 0.4% *trans*-2-ene, and 0.1% butane. The analysis of the *cis*-2-butene was

	<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂
Obsd.	0.386	0.465	0.149
Random	0.383	0.472	0.146

Initial State of Catalyst.—On certain occasions, the 50-cc. tube containing an initial sample or one collected after a temperature change was found to contain substantial quantities of both butane and butyne. For *H* near 1.0, gas entered the 50-cc. tube at the rate of 18 cc. per minute. With no back mixing in the tube, it would take about 3 min. to sweep out the former contents. If, as is probable, there was back mixing the sweep-out time would be longer. If, now, the value of *H* crossed 1.0 during the collection period, one would find both butyne and butane in the tube even if the catalyst was 100% selective. In run 36 with 0.388 g. of fresh catalyst at 26°, samples were collected both by the 50-cc. collection tubes and by the gas syringe for which the collection problem should be much less serious. Results are given in Table II.

TABLE II
ANALYSES OF RUN 36

Time, min.	Sampling	2-Butyne, %	<i>cis</i> -2-ene, %	<i>trans</i> -2-ene, %	1-ene, %	ane, %
0-2.5	Tube	0.0	11.5	22.6	1.1	64.8
3.5	Syringe	13.1	82.5	3.0	1.0	0.4
15.5	Syringe	52.5	46.4	0.5	0.3	.3
9-15	Tube	42.8	55.8	0.6	0.4	.4

The transient initial state of the catalyst was investigated by an arrangement in which the hydrogen-butyne flow was separately established but vented. At time, *t*₀, the hydrogen-butyne flow was started over the catalyst which had been standing in hydrogen. Samples were removed *via* syringes at short time intervals. The results of run 47 at 29° with 0.200 g. of fresh catalyst are given in Table III.

In the similar run 70, 0.023 g. of fresh catalyst was employed. The 5-12 and 14-21-sec. samples contained no hydrocarbon. The 25-38-sec. sample contained 4.3% *cis*-, 0.2% *trans*-2-butene, and 0.4% butane. The 65-80-sec. sample contained 2.2% *cis*-2-butene.

TABLE III
INITIAL BEHAVIOR OF CATALYST IN RUN 57

Time, ^a sec.	2-yne, %	cis-2-ene, %	trans-2-ene, %	1-ene, %	-ane, %	Sample ^b content
15-35	0.0	0.0	0.0	0.0	100	0.3
37-60	0.0	31.4	49.6	2.9	16.1	12.9
62-78	15.4	82.3	1.5	0.3	0.5	16.2
78-93	40.9	57.7	1.1	0.1	0.2	13.4

^a 2-cc. samples of gas were removed during the seconds after start shown in this column. ^b Approximate relative value of total hydrocarbon in the sample.

Reaction in Liquid Phase.—Hydrogenation of 3-hexyne was investigated with 140-200 mesh 13.8% palladium-on-alumina at 0 and 25° and the addition of deuterium at 0°. Two to five samples were taken during the course of a run and certain were selected for detailed analysis. Typical chemical analyses are given in Table IV.

TABLE IV
HYDROGENATION OF 3-HEXYNE

H	Temp., °C.	Hydrocarbon fraction						
		3-yne	cis-3	trans-3	cis-2	trans-2	1-ene	-ane
0.048	27	0.952	0.048					
.127	0	.873	.118	0.005	0.001	0.001	0.000	0.001
.206	24	.799	.181	.011	.002	.002	.000	.005
.350 ^a	0	.658	.317	.012	.003	.004	.000	.007
.678	0	.333	.608	.028	.009	.009	.000	.012
.750	24	.268	.666	.034	.013	.008	.000	.010
1.080	27	.000	.456	.257	.064	.141	Tr.	.082
1.283	0	.000	.042	.301	.070	.304	Tr.	.283
Equil. ^b			.017	.208	.139	.621	0.006	

^a Deuterium used as reductant. ^b Best available estimate of equilibrium in the hexenes at about room temperature: T. M. O'Grady, R. M. Alm, and M. C. Hoff, Preprints, Division of Petroleum Chemistry, American Chemical Society, Vol. 4, No. 4, B-65 (1959).

In run 96 with deuterium at 0°, the unreacted 3-hexyne was devoid of deuterium. The *cis*-3-hexyne was isolated and analyzed mass spectrographically for two samples as shown in Table V.

TABLE V
DEUTERIUM DISTRIBUTIONS IN *cis*-3-HEXYNE

H	d ₀	d ₁	d ₂	d ₃	d ₄	d _{av}
0.154	0.010	0.106	0.873	0.008	0.004	1.89
.350	.008	.106	.871	.010	.005	1.90

The half-life of the hydrogenation at 0° was about 1 hr. and the kinetics seemed close to zero order. We ran into difficulties with poisoning when we attempted to use less than 10 mg. of catalyst. Since 10 and 20 mg. of catalyst gave about the same rate, hydrogen transfer from the gas phase may have been rate limiting. This point was not investigated carefully since it seemed irrelevant to our results.

In the run at $H = 0.350$, the small amount of hexane was isolated and examined mass spectroscopically. The isolated amount was so small that much reduced sensitivity resulted and tenths of % are not significant. The analysis gave: d_2 1.6%, d_3 12.5, d_4 51.2, d_5 9.9, d_6 6.1, d_7 4.1, d_8 5.6, d_9 6.4, d_{10} 1.0, d_{14} 1.5. The missing d 's are less than 1%. The computed d_{av} is 4.9.

Discussion

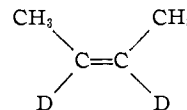
The 0.03% palladium-on-alumina is a very active catalyst for the hydrogenation of 2-butyne. At 25°, about 0.1 g. of this catalyst leads to the hydrogenation of half of the 2-butyne flowing at the rate of 0.022 mole per hr. Thus, each atom of palladium leads to the reaction of 10 molecules of 2-butyne per sec. Considering that two palladium atoms probably constitute a site and that not all of the palladium atoms are available, the turn-over number is probably closer to 100. If, as well may be, much of the surface of the palladium

is covered with relatively slowly reacting species, the turn-over number may be even greater. Thus, the activity of the catalyst corresponds to that of one of the more active enzymes.

It is this high activity which forces us to use such a dilute catalyst in order to keep the reaction under control and to get values of H (moles of hydrogen added per molecule of 2-butyne) less than 2.00. However, from our previous comparison of this catalyst with palladium film,³ we believe that this dilute catalyst has the general characteristics of palladium.

Although the reactions are very fast, there are no serious concentration gradients in the catalyst pores. Suppose that there were. The concentration of the more slowly diffusing butyne would go to zero before the center of the catalyst particle was reached. In the inner portions of the catalyst, *cis*-2-butene would hydrogenate and isomerize. This is inconsistent with the high selectivity of the reaction and with the lack of variation with conversion of the ratios of butane and of the other butenes to *cis*-2-butene. The formation of these by-products probably accompanies the original hydrogenation of 2-butyne.

As may be seen from Table I, the heavily predominant product of the addition of deuterium to 2-butyne is *cis*-2-butene- d_2 . At 14°, 99% of the product is *cis*-2-butene and only about 0.2% of this has more than two deuterium atoms. The finite values of d_1 and d_0 largely result from the hydrogen content of the deuterium employed. Nuclear magnetic resonance shows that the two deuterium atoms are located at carbon atoms 2 and 3. Thus, the product is 99%



Once all butyne has reacted, this compound further reacts as will be reported in a subsequent paper.

At higher temperature (Table I), the selectivity declines somewhat and the amount of multiply exchanged *cis*-2-butene increases, but even at 58° the reaction gives remarkably simple products.

At 15° in the absence of 2-butyne a mixture of H_2 and D_2 undergoes nearly equilibrium isotopic exchange, $H_2 + D_2 = 2HD$, at our ordinary flow rates. In the presence of butyne this reaction is very heavily inhibited; only about 3% HD is formed. The reduction in rate is by a factor of 40 or greater. However, as reported in the Experimental section, the distribution of deuterium in the resultant *cis*-2-butene is random. Thus, hydrogen must be dissociatively adsorbed and scrambled on the palladium surface before reaction with butyne.

These reactions with mixtures of hydrogen and deuterium resemble those reported for the hydrogenation of ethylene on nickel: inhibition of the hydrogen-deuterium exchange reaction (or the equivalent parahydrogen conversion) and formation of the same product from the hydrogenation of ethylene with $H_2 + D_2$ or with the pre-equilibrated mixture of $H_2 + HD + D_2$.⁶ The very low rate of desorption of HD is presumably the result of two factors, the small fraction of surface available for adsorption of hydrogen and the lowering of the coverage on this fraction by rapid reaction with the adsorbed, unsaturated species.

Although the isotopic distribution pattern of *cis*-2-butene is random, an incorporation isotope effect favors addition of hydrogen over that of deuterium by

(6) For a review of this matter see D. D. Eley, "Catalysis," edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., Vol. III, 1955, pp. 63 and 66.

a factor of 1.6. Since negligible quantities of hydrogen desorb, hydrogen which adsorbs leaves the surface only as *cis*-2-butene. Thus, the isotope effect refers to the relative rates of adsorption of hydrogen and deuterium from the gas phase (or perhaps from a weak, equilibrium adsorption). There may well be a subsequent isotope effect in the reaction of adsorbed hydrogen atoms, but this is not reflected in the number, 1.6.

Attempts were made to measure the kinetic isotope effect on the rate of the reaction by the alternation hydrogen, deuterium, hydrogen. Because of activity drift, really accurate values were not obtained, but the isotope effect is near 2.0 with hydrogen faster.

Reaction in Liquid Phase.—As may be seen from Table IV, the hydrogenation of 3-hexyne is rather selective and stereoselective. The selectivities are the same at 25 and 0° and the same with hydrogen and deuterium. The products are *cis*-3-hexene, 91.2%; *trans*-3-hexene, 4.3%; *cis*-2-hexene and *trans*-2-hexene, 1.4% each; and hexane, 1.6%.⁷

As shown in Table V, the isotopic distribution pattern is rather simple. Less than 2% of the *cis*-3-hexene has exchanged additional hydrogen atoms and the unreacted 3-hexyne has no deuterium. The patterns resemble those of 2-butyne in gas phase reaction (Table I) except for the larger values of d_1 and the consequent smaller values of d_{av} . The missing deuterium is presumably stored in the small quantities of the other products. We were able to isolate the hexane from the run in Table IV at $H = 0.35$. It had a wide isotopic distribution and a d_{av} of 4.9. Consequently, in its formation, hydrogen atoms had been transferred to the surface and then incorporated into *cis*-3-hexene.

Once all hexyne has reacted, the *cis*-3-hexene hydrogenates and isomerizes as shown in the two entries in Table IV at H greater than 1.0. At $H = 1.28$, the distribution of hexenes is approaching equilibrium.

On the whole, then, the products of hydrogenation of disubstituted acetylenes in vapor and in liquid phase are very nearly the same. It seems likely that the same mechanism is involved in both reactions. What is the origin of the only substantial difference in detail, the lower stereoselectivity in the liquid phase? In the vapor phase, all parts of the catalyst are supplied with an excess of hydrogen owing to the excess of hydrogen in the reactant mixture and to the higher diffusivity of hydrogen. In the liquid phase, the hydrogen concentration in the liquid phase is low. Thus, even if hydrogen has the higher diffusivity, it will be the first exhausted as one proceeds into a catalyst pore. The greater degree of isomerization of *cis*-3-hexene may well

(7) Rather similar results for Raney nickel have been reported: L. Kh. Freidlin, Yu. Yu. Kaup, E. F. Litvin, and T. I. Ilomets, *Proc. Acad. Sci. USSR, Chem. Sect.*, **143**, 293 (1962).

be connected with this. However, this isomerization accompanies the original act of hydrogenation and is not due to subsequent adsorption of *cis*-3-hexene since the product ratios are independent of conversion.

Steady State.—In previous work³ we frequently observed that initial samples of reaction products contained 2-butyne as well as butane and *trans*-2-butene. We ascribed this to a surface reaction which transformed an initially unselective catalyst to a selective one. The experiments described in the Experimental section suggest another explanation.

The initial activity of the catalyst is generally higher than that after a few minutes. As shown in Table II, the product collected over the first 2.5 min. was typical of that for a reaction with $H = 1.65$. Yet 1 min. later a sample collected very rapidly showed unreacted butyne and nearly normal selectivity. Similar behavior is shown in Table III in which a series of short-period samples were collected. Within 1 min., the reaction product went from butane only to excess butyne and nearly normal selectivity. Further, where the catalyst quantity was so low that steady-state conversions would be but a few %, the first samples collected were essentially devoid of butane and exhibited normal selectivity.

The initial high activity cannot be due to reaction of hydrogen adsorbed on or dissolved in the palladium since over 100 molecules of 2-butyne must have reacted per palladium atom during the initial period of the reactions of Tables II and III.

We suggest that the catalytic activity declines during the first minute consequent either to removal of dissolved hydrogen or to partial coverage of the surface by slowly reacting residues. If initially H is less than unity, the catalyst is nearly selective initially. Our former samples indicative of low selectivity were, then, mainly an artifact of sample collection during a period in which H crossed unity. Our data do, however, suggest that there may be a small increase in catalyst selectivity over the first 10 min. or so.

Mechanism.—For a heterogeneous catalytic reaction on a transition metal these results are of almost unparalleled simplicity. The addition of deuterium to *cis*-2-butene, for example, would be accompanied by isomerization and by a seriously smeared isotopic distribution pattern of the butane product.⁸ Details of the mechanism will be discussed in the following paper.

Acknowledgment.—This research was supported by the Air Force Office of Scientific Research (Directorate of Chemical Sciences).

(8) See G. C. Bond, "Catalysis by Metals," Academic Press, Inc., London, 1962.