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The Isomerization of Propyne into Propadiene Over a Silica Catalyst

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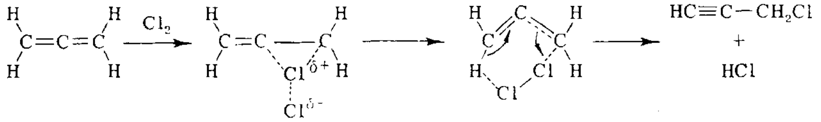
Propyne was isomerized to propadiene over a silica catalyst labeled with tritium. We could demonstrate that for every isomerizing molecule a hydrogen atom of the catalyst is exchanged; the propadiene which was formed contained the calculated amount of tritium. For the reverse reaction, however, it was found that the methyl group of propyne contained only about 40% of the expected amount of tritium, probably owing to an isotope effect.

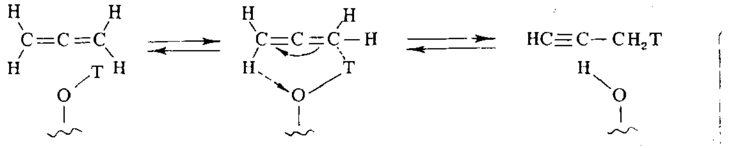
The results are explained in terms of a tentative reaction mechanism. The empirical activation energy for the isomerization reaction is 13 kcal/mole.

1. INTRODUCTION

In a previous article in this series (*1*), it was found that, upon chlorination of propadiene, propargyl chloride is formed beside 2, 3-dichloropropene. Formation of the former was interpreted in terms of a four center (type) addition/elimination reaction (l.c.) as represented below:



In order to investigate whether other reactions of propadiene can be explained by a similar mechanism, we studied the isomerization of propadiene to propyne over a SiO_2 catalyst, labeled with tritium. The isomerization was described earlier by Slobodin (*2*) and later on, more thoroughly, by Cordes and Güntzler (*3*). The mechanism may be represented as follows:



Comparison of the rate of tritium incorporation into the methyl group of propyne or, for the reverse reaction, into propadiene with the rate of isomerization may help to elucidate the reaction mechanism involved.

2. DESCRIPTION OF EXPERIMENTS

As a first step, we developed a reproducible procedure for labeling the catalyst, containing reactive hydrogen atoms, with tritium, and we ascertained that this labeled product, under the reaction conditions used, did not lose its hydrogen (tritium) by other causes than the reaction(s) with propadiene or propyne. Secondly, a suitable reaction temperature was sought. It was found that at 250° reasonable conversions were obtained and side-reactions were practically negligible. Therefore, all experiments were carried out at this temperature.

The propadiene/propyne mixture led

over the labeled SiO_2 catalyst was separated by preparative gas chromatography. Radioactivity of both hydrocarbons was measured in an ionization chamber. To localize the activity in the propyne fraction, the propyne was precipitated as the silver salt, and regenerated with NaCN. Radioactivity measurements of the propyne before and after this procedure gave the distribution of activity in the molecule. As a matter of course, corrections were made for direct hydrogen exchange without isomerization. Results are given in Sect. 4.

3. Experimental Part

3.1. Preparation of Labeled Catalyst

The SiO_2 catalyst was prepared as follows: 12 liters of distilled water were added to 1.2 liters of water-glass. Then, 1600 ml of 2.5 N HCl was added with stirring. SiO_2 precipitated. Next, 3 liters of 0.25 N HCl were added.

The precipitate was centrifuged and washed six times with 10 liters of distilled water and twice with 10 liters of 0.05 N HCl. 1.4 kg product was obtained which was air dried for 3 hr at 300°. 100 g of this powder were stirred for 1 hr with 200 ml of tritiated water ($\sim$16 μCi/ml). The residue was dried over P_2O_5 and heated for 3–5 hr at 500° in a tube-furnace. During the drying procedure a preheated, dry stream of nitrogen was led over the solid mass. To determine the activity of the powder a weighed amount was stirred with twice its weight of water. The activity of the water was determined by liquid scintillation counting. The specific activity of the powder was independent of the length of the exchange or re-exchange time with water. Exchange was complete within 3 min (measured within 3 and 60 min).

Drying for 3 or 5 hr in an N_2-stream at 300° made no difference as to the tritium content.

3.2. Isomerization of Propadiene at Different Temperatures

The apparatus used is given schematically in Fig. 1. Propadiene entered the tube-furnace at a rate of 37 ml/min; 15 g of catalyst was used. This catalyst was always placed in that part of the tube furnace where the temperature was con-

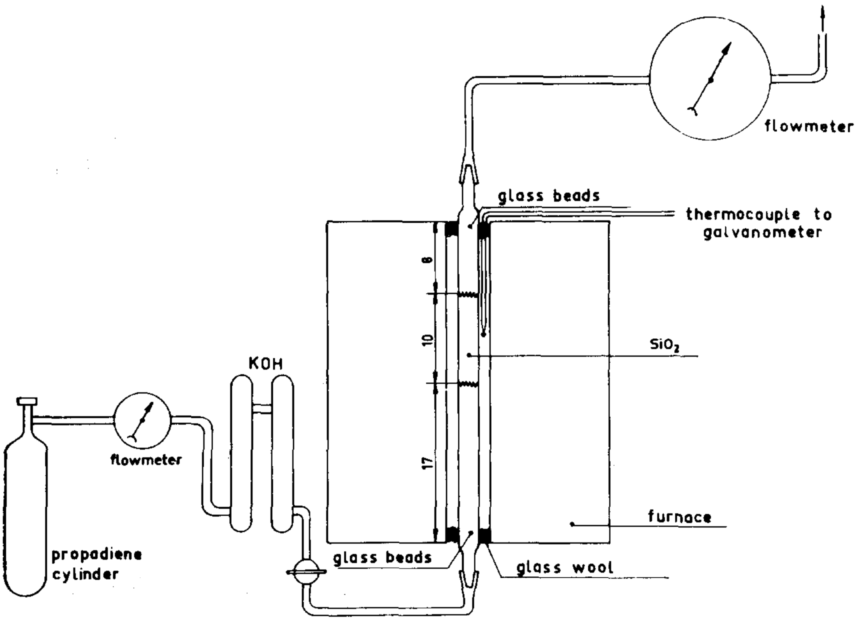


FIG. 1. Apparatus used in the investigation of propadiene–propyne isomerization.

stant.* During the warming-up of the furnace the complete apparatus was filled with nitrogen. The yields of propyne were determined by analytical gas chromatography.

3.3. Isomerization Over Labeled Catalyst at 250°

In Expts. 1 and 2, propadiene was led for 75 min over about 15 g of catalyst, at a rate of 37 ml/min, at 250°. The gas mixture flowing out during the first 30 min was led over P_2O_5, condensed at —80°, and separated on a preparative scale with a gas chromatograph (see below). The composition of the mixture (and the purity of the fractions obtained after the preparative separation) was determined gas-chromatographically on an analytical column (see below). Next, the specific activities of both fractions were measured in a 100-ml ionization chamber.

In Expts. 3 and 4, propyne was led over the catalyst at 250°. Experiment 5 (with propadiene) and Expt. 6 (with propyne) were carried out in the same way as 1, 2, 3, and 4, with the difference that the gas mixtures flowing out during the first 15 min were collected. Numerical data and results of these 6 experiments are given in Table 2 and Sect. 4.3.

3.4. Distribution of Tritium in Propyne

By warming up, the condensed propyne fraction was led slowly into a well-stirred mixture of 50 ml of 20% $AgNO_3$ and 50 ml of 95% ethanol. After leading all the propyne into the mixture, nitrogen was passed during 30 min through the apparatus, after which the reaction mixture was left to itself for another 30 min. The precipitate was filtered off. The propyne–Ag complex was transferred with the filter to a 50-ml two-necked flask and about 30 ml of water were added; the suspension was then heated to 50° on a water bath. Next, 10 ml of a 25% NaCN solution was added in about 15 min. The flask was connected via a coiled distillate condenser (—15°) to two condensing tubes that were kept at —10 and —80°, respectively. After adding all the NaCN, nitrogen was passed through the flask. The activity of the regenerated propyne was then measured again in the ionization chamber.

3.5. Gas-Chromatographic Separation of Propadiene–Propyne Mixtures

3.5.1. Analytical separation. Propadiene/propyne ratios were determined by GLC over an 8-m copper column (i.d., 4 mm). The carrier was Supercel C 22 (40–60 mesh), the stationary phase trioctyl phthalate (TOF), the percentage of TOF in the filling, 20%. Hydrogen was used as elution gas. The separation was carried out at room temperature. The amount of injected mixture was 10 ml. The detection was carried out with a katharometer.

3.5.2. Preparative separation. The preparative separations were carried out with a copper column, length 6 m (i.d., 13 mm). The carrier was Supercel C 22; the stationary phase, dimethyl sulpolane 20% (w/w); the fractions were condensed at —190° (liquid nitrogen) into 3 U-tubes placed in series, and filled with glass beads. Flow rate, 400 ml/min. The separation was carried out with about 2 g of the mixture.

The detection was carried out with a katharometer which in this case gave only qualitative information. The purity of the fractions was checked with the analytical column as described above.

3.6. Ionization Chamber Measurements

The activity of the gas fractions was measured in a 100-ml ionization chamber (Frieseke and Hoepfner FH 56/Z 2). The ionization current was measured across a resistance of 10^{12} Ω with a Vibron electrometer No. 33 C. A U-tube with a condensed fraction was connected to the small vacuum line (Fig. 2). The liquid was frozen with liquid nitrogen, the system was evacuated (~0.05 mm) and next, part of the gas was admitted to the ionization chamber by slowly warming up the U-tube. Pressures were measured with manometer M and

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* In the radioactive experiments, the filling of the reactor tube with SiO_2 was carried out in a dry box.

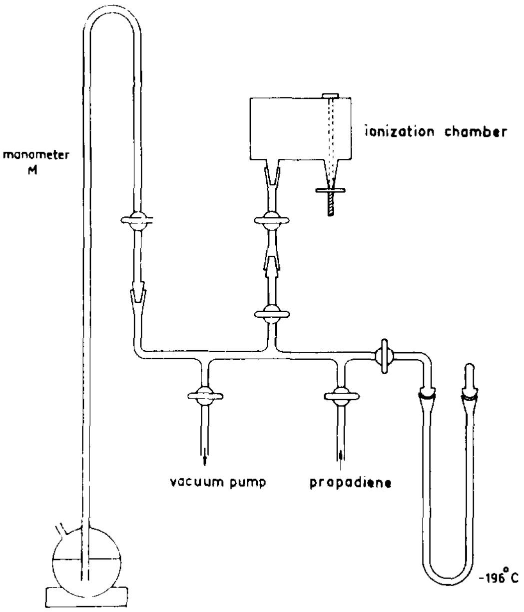


FIG. 2. Vacuum line and ionization chamber for the measurements of the radioactivity of propadiene and propyne.

read with a cathetometer. Next the chamber was filled up with inactive propadiene (also in the case of propyne) until the pressure was 75 cm. The ionization chamber was calibrated, with propadiene as a filling gas. One μCi of tritium gave rise to a voltage of 706 mV across a resistance of $10^{12}\,\Omega$, at 20°.

4. RESULTS AND DISCUSSION

4.1. Energy of Activation

The results of the isomerization of propadiene at 5 different temperatures are given in Table 1. From these data an experimental energy of activation for the isomerization reaction of propadiene to propyne can be estimated. The Arrhenius plot is linear with an activation energy of 13 kcal/mole.

TABLE 1
PERCENTAGE OF PROPYNE, GENERATED BY ISOMERIZING PROPADIENE, AS A FUNCTION OF THE TEMPERATURE[a]

t (°C)	200	225	250	275	300
Propyne (%)	3.5	6.2	11.5	22.0	33.3

[a] Flow rate at inlet, 37 ml/min; flow rate at outlet, 38.8 ± 1.3 ml/min; Time of contact = (vol of contact space − vol of catalyst)/[vol of gas/sec (corr. for temp)] = 18.2 ± 1.8 sec.

4.2. Activity of the Catalyst

The specific activity of the hydrogen in the catalyst, as determined by exchange with an excess of water (cf. 3.1), was 144 ± 5 nCi/mmole of H. This activity is, after correction for dilution, equal to the specific activity found for the acetylenic hydrogen in the various experiments (Table 2). Therefore, it can be inferred that the acetylenic hydrogen is in rapid equilibrium with the hydrogen of the catalyst, and in the remaining further calculations it is assumed that the specific activity of the hydrogen of the catalyst has the same value as the specific activity of the acetylenic hydrogen.

4.3. Incorporation of Tritium During Isomerization

The results of the isomerization experiments over a tritium-labeled SiO_2 catalyst are summarized in Table 2. To determine the degree of tritium incorporation during isomerization, it is necessary to make a correction for tritium exchange without isomerization. For this purpose we consider the activities of the unchanged molecules after passage over the catalyst. (Since in all cases equilibrium is far from being attained, i.e., the propyne:propadiene ratio is about 4:1, the reverse reaction may be neglected.) In addition, it may be assumed that, on the average, an isomerized molecule was in the form of propadiene during half the contact time, and during the other half in the form of propyne, and that the activity taken up from the catalyst is proportional to the contact time.

During the full contact time, the hydrogen atoms of propadiene are exchanged with those of the catalyst, resulting in a specific activity of 13 nCi/mmole of H (Table 2, Expts. 1 and 2), and for the methyl group of propyne, 8.5 nCi/mmole of H (Expts. 3 and 4). Since an isomerized molecule was in the form of propadiene only during half the contact time, each hydrogen atom is exchanged with tritium

TABLE 2

PROPADIENE–PROPYNE ISOMERIZATION OVER A TRITIUM-LABELED SiO_2 CATALYST

Sp act, approx 144 nCi/mmole of H; flow rate, 37 ml/min; temp 250°

Gas led over the catalyst:	Propadiene		Propyne		Propadiene	Propyne
Expt.:	1	2	3	4	5	6
Weight of catalyst (g)	15.2	15.8	17.1	16.3	15.0	15.1
Total activity in catalyst (μCi)	14.6	11.1	12	11.4	9.6	9.7
Amount of gas collected after reaction (ml)	820	820	820	820	443	352
Propadiene and propyne (%), respectively, in exit gas mixture	75/25	68/32	9/91	11/89	62/38	10/90
Sp act (nCi/mmole of H)						
hydrogen in propyne	52	44	35	34	52	41
H in the CH_3-group	28	24	8	9	29	9
acetylenic H	122	103	117	112	121	138
H in propadiene	12	14	63	60	15	75

for 6.5 nCi/mmole of H. Two of the three hydrogen atoms of the methyl group in propyne originate from propadiene. In the form of propyne, another 4.3 nCi/mmole of H (half of av found in Expts. 3 and 4 in Table 2) are taken up, totalling 10.8 nCi/mmole of H. The third hydrogen atom in the methyl group of propyne originates from the catalyst (112.5 nCi/mmole). In the case of complete exchange with the catalyst during isomerization of propadiene to propyn, the specific activity of the methyl group would be $(112.5 + 2 \times 10.8)/3 = 44.7$ nCi/mmole of H. This is roughly twice the experimental value (26 nCi/mmole of H).

Apparently, during the isomerization step hydrogen is preferentially taken up from the catalyst as compared to tritium, resulting in an isotope effect of approximately 2. Due to this phenomenon, the specific activity of the third hydrogen atom in the methyl group of propyne originating from the catalyst is only about half of the specific activity of the hydrogen atoms of the catalyst. Therefore, additional exchange with the catalyst without isomerization can take place, resulting in an extra correction factor of $4.3/2 = 2.2$. nCi/mmole of H. The total correction for tritium exchange without isomerization in the methyl group of propyne is therefore: $2 \times 10.8 + 2.2 = 23.8$ nCi/mmole of CH_3. Similar corrections are made for Expts. 3, 4, 5, and 6. The results of the calculations are presented in Table 3.

4.4. Mechanism of the Isomerization Reaction

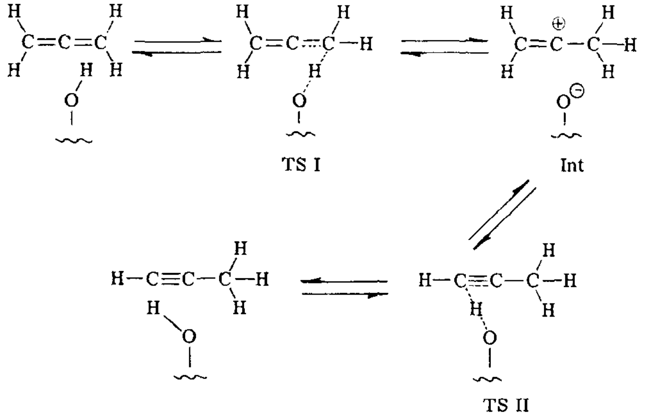
In the isomerization reaction propadiene–propyne over a tritium-labeled SiO_2 catalyst, three kinds of hydrogen exchange have been observed. First, instantaneous exchange takes place with the acetylenic hydrogen atom of propyne. This is not unexpected, considering the acidity of this

TABLE 3

COMPARISON OF CALCULATED AND EXPERIMENTAL DATA OF THE SPECIFIC ACTIVITIES OF THE PROPYNE METHYL GROUP AND OF PROPADIENE, CAUSED BY ISOMERIZATION

Sp act (nCi/mmole)	In propyne-CH_3		In propadiene	
Expts.:	1, 2	5	3, 4	6
Found (cf. Table 2)	78	87	246	300
Correction for exchange without isomerization	24	26	136	162
After correction	54	61	110	138
Expected (= sp act, acetylenic H)	113	121	114	138
Isotope effect k_H/k_T	2.1	2.0	1.0	1.0

group. Secondly, tritium incorporates—without isomerization—into propadiene at a greater rate than into the methyl group of propyne. A correction for these effects has been made for the evaluation of the third kind of hydrogen exchange which occurs during the isomerization. Abstraction of a tritium atom from the catalyst may be expected to be subject to a primary isotope effect. The maximum value for this effect may be estimated (*4*) as $k_H/k_T = 7.3$, assuming a value of 3738 cm^{-1} for the stretching frequency of the OH-bond in the catalyst (*5*). Indeed, such an effect has been observed for the reaction of propadiene to propyne, k_H/k_T being 2.0. However, the reverse reaction of propyne to propadiene shows no isotope effect. This means that hydrogen abstraction from the catalyst is rate-determining only in the isomerization of propadiene. Therefore, a four center (type) reaction, or any mechanism in which only one transition state is involved, may be ruled out.* A reaction profile as represented in Fig. 3 is in agreement with the observed data. The following reaction mechanism agrees with this energy profile:



The intermediate Int may be visualized as an ion pair. In TS I, which corresponds to the rate determining step, an O–H bond of the catalyst is broken by propadiene. However, starting from propyne, a C–H bond of the methyl group is broken in TS I. Therefore, in the case of a tritiated catalyst, a primary isotope effect may be expected for the isomerization of propadiene, whereas the reverse reaction will exhibit no isotope effect.

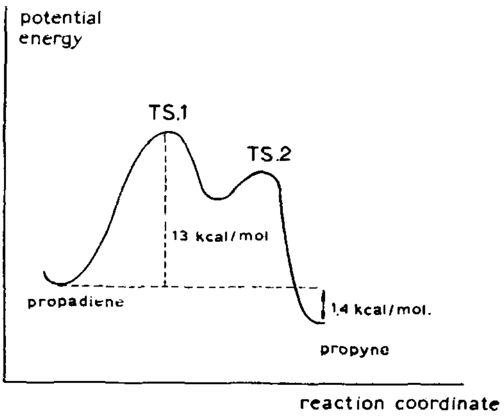


FIG. 3. Potential energy profile of the isomerization reaction propadiene-propyne.

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* An intramolecular hydrogen-shift might also account for this apparent isotope effect. However, the role of the catalyst is unclear in such a mechanism. Yet no uncatalyzed isomerization has been observed under these conditions. Moreover, in this case the absence of a primary isotope effect would have to be explained.