Chemistry

V. M. Gryaznov and V. I. Shimulis

1961

SovietRxiv

Abstract

Full Text

Chemistry

V. M. Gryaznov and V. I. Shimulis

On the Mechanism of the Transformations of Cyclohexene and 1,3-Cyclohexadiene on Platinum Films

(Presented by Academician A. A. Balandin, 10 I 1961)

The processes of redistribution of hydrogen between molecules of one and the same substance, not accompanied by evolution of gas, were discovered in 1911 and subsequently studied in detail by N. D. Zelinskii and his school (^1). In particular, it was established that 1,3-cyclohexadiene is transformed at a high rate according to the equation

$$2C_6H_8 = C_6H_6 + C_6H_{10}, \tag{1}$$

whereas cyclohexene reacts much more slowly according to the equation

$$3C_6H_{10} = C_6H_6 + 2C_6H_{12}. \tag{2}$$

On the basis of the data then available, A. A. Balandin (^2) attempted to explain the distinctive features of these reactions by means of models according to which, on one or two—in the case of reaction (2)—triplets, direct transfer of hydrogen atoms between molecules takes place. Linstead and his co-workers (^3) later came to the conclusion that hydrogen is transferred directly, whereas N. A. Shcheglova and M. Ya. Kagan (^4) believed that the redistribution of hydrogen in cyclohexene consists of separate stages of dehydrogenation and hydrogenation.

In view of the existence of several concepts concerning the mechanism of hydrogen redistribution, it is desirable to obtain data that reveal it as directly as possible. The present communication is devoted to the results of studying the transformations of cyclohexene and 1,3-cyclohexadiene* at 20° on platinum films, the electrical conductivity of which was measured in the course of the experiments.

The experimental procedure did not differ from that used in works ([6-10]), where it was shown that adsorption of benzene, cyclohexane, cyclohexene, and 1,3-cyclohexadiene can be subdivided into strong adsorption, not removed by prolonged evacuation to $1 \cdot 10^{-7}$ mm at 20°, and reversible adsorption. Upon the first admission onto a freshly prepared platinum film, all the hydrocarbons listed

Fig. 1. Dependence of the amount of hydrogen formed N_{H2} (1) and of the ratio $N_{H2}/N_{C6H_{10}}$ on the amount of cyclohexene $N_{C6H_{10}}$ admitted into the vessel with the film (2)

Figure 1: Fig. 1. Dependence of the amount of hydrogen formed N_{H2} (1) and of the ratio $N_{H2}/N_{C6H_{10}}$ on the amount of cyclohexene $N_{C6H_{10}}$ admitted into the vessel with the film (2)

are strongly adsorbed and at the same time undergo dehydrogenation. Especially large amounts of hydrogen are evolved during the strong adsorption of cyclohexene and cyclohexadiene.

The reversible adsorption of benzene and cyclohexane is not accompanied by dehydrogenation, whereas cyclohexene and cyclohexadiene lose hydrogen even under these conditions, as indicated by the appearance in the adsorption vessel of a gas that does not condense at the temperature of liquid nitrogen and that, in the experiments described below, hydrogenated cyclohexene. Changes in the electrical conductivity of the film during the reversible adsorption of cyclohexene also revealed the presence of hydrogen. Consequently, the evolution of hydrogen as a result of the strong adsorption of benzene and cyclohexane on platinum films is due to chemisorp–

* The constants of the hydrocarbons used–C_6H_{10}, b.p. 82.5°, n_D^{20} 1.4448, d_4^{20} 0.812; C_6H_8, b.p. 78.5/740 mm, n_D^{20} 1.4740–were in satisfactory agreement with literature data (^5): C_6H_{10}, b.p. 83°, n_D^{20} 1.44507, d_4^{20} 0.8102; C_6H_8, b.p. 80.5°, n_D^{20} 1.4744.

tion, and in the cases of cyclohexene and cyclohexadiene it is a catalytic process that occurs when the vapors are admitted after evacuation of the film.

If the supply of cyclohexene or cyclohexadiene vapors is periodically interrupted and the hydrocarbon vapors are frozen out of the gas phase, it can be found that the amount of hydrogen formed passes through a maximum. In particular, with cyclohexene curve 1 in Fig. 1 was obtained, while curve 2 shows the dependence of the ratio of the numbers of hydrogen and cyclohexene molecules, $N_{H2}/N_{C6H_{10}}$, on the number of admitted cyclohexene molecules. The results of experiments with cyclohexadiene were analogous, but approximately 2 times less hydrogen is evolved than upon adsorption of the corresponding amount of cyclohexene. Thus, after admitting $1 \cdot 10^{17}$ cyclohexene molecules onto a film containing $3.5 \cdot 10^{16}$ platinum atoms per 1 cm^2, the pressure of the hydrogen evolved was $2.5 \cdot 10^{-3}$ mm. To attain a similar pressure ($2 \cdot 10^{-3}$ mm), it was necessary to admit $2.1 \cdot 10^{17}$ cyclohexadiene molecules onto the same film after its evacuation.

Fig. 1. Dependence of the amount of hydrogen formed N_{H2} (1) and of the ratio $N_{H2}/N_{C6H_{10}}$ on the amount of cyclohexene $N_{C6H_{10}}$ admitted into the vessel with the film (2)

To determine the reasons for the decrease in the ratio $N_{H2}/N_{C6H_{10}}$ with increasing $N_{C6H_{10}}$, a series of experiments was carried out in each of which $2.8 \cdot 10^{16}$ cyclohexene molecules were admitted at a constant rate of $1.4 \cdot 10^{15}$ molecules/min into a vessel with a platinum film containing various amounts of hydrogen. The results of experiments with a film having a density of $2.2 \cdot 10^{16}$ Pt atoms per 1 cm^2 are presented in Table 1. Before all the experiments, except the tenth, the vessel was evacuated to a residual pressure of about $5 \cdot 10^{-7}$ mm.

Experiments Nos. 1 and 2 show the reproducibility of the percentage dehydrogenation of cyclohexene. From experiments Nos. 3-10 it is seen that, at a definite amount of hydrogen in the adsorption vessel, which in this case is close to $7.9 \cdot 10^{16}$ molecules, admission of $2.8 \cdot 10^{16}$ cyclohexene molecules does not lead to evolution or absorption of hydrogen. If there is less or more hydrogen than this amount, then upon admission of cyclohexene hydrogen is, respectively, either evolved or absorbed. Cyclohexadiene is likewise capable not only of being dehydrogenated but also of being hydrogenated on a platinum film at 20°. Thus, in one of the experiments, after admission of $1.5 \cdot 10^{17}$ cyclohexadiene molecules, the hydrogen pressure in the adsorption vessel with the platinum film increased from $8 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ mm, whereas in the case when the hydrogen pressure over the same film was, before admission of the hydrocarbon, $1.2 \cdot 10^{-2}$ mm, after admission of $2.0 \cdot 10^{17}$ cyclohexadiene molecules it decreased to $9 \cdot 10^{-3}$ mm.

These results show that on platinum films at 20°, hydrogenation and dehydrogenation of both cyclohexene and cyclohexadiene occur simultaneously. When the first portions of these hydrocarbons are admitted, dehydrogenation predominates, while as hydrogen accumulates the rate of hydrogenation increases. If the rates of these processes became equal, then the amount of hydrogen in the vessel, having reached a certain value, would not change with further admission of hydrocarbon. In reality, however (see Fig. 1, curve 1), the amount of hydrogen passes through a maximum. Consequently, the ratio of the rates of hydrogenation and dehydrogenation increases. This is also indicated by the results of experiments Nos. 7-10 (Table 1). In experiments Nos. 7-9 the consumption of hydrogen regularly decreased with decreasing init-

amount of hydrogen, while in experiment No. 10, where a further decrease should have been observed, there was an increase in hydrogen consumption. As already mentioned, before experiment No. 10 the products of experiment No. 9 had not been pumped off.

It is natural to assume that the observed predominance, at certain amounts of hydrocarbons, of the rate of hydrogenation of cyclohexene or cyclohexadiene over the rate of dehydrogenation is due to selective blocking of those regions of the film surface on which dehydrogenation takes place. Dehydrogenation and hydrogenation occur under reversible adsorption of cyclohexene or cyclohexadiene, when decyclization and cracking reactions are unlikely. Under these conditions the only stable products of the transformation can be benzene and

cyclohexane, which, under reversible adsorption on platinum films at 20°, are not dehydrogenated. It remains to determine how their presence affects the ratio of the rates of hydrogenation and dehydrogenation of cyclohexene.

Table 1

Changes in the amount of hydrogen in the vessel with the film after admission of $2.8 \cdot 10^{16}$ molecules of cyclohexene

Experiment Nos.	1	2	3	4	5	6	7	8	9	10
Before admission	0	0	2.7	6.3	8.0	7.9	37.4	33.3	30.8	29.8
After admission	2.7	2.7	1.6	1.1	−0.1	0	−4.1	−2.5	−1.0	−2.5

Table 2

Transformations of cyclohexene on a platinum film in the presence of cyclohexane and benzene

Experiment No.	$N_{H2} \cdot 10^{-16}$ before experiment	Vapor pressure, mm C_6H_{12}	Vapor pressure, mm C_6H_6	$N_{C_6H_{10}} \cdot 10^{-16}$	$N_{H2} \cdot 10^{-16}$ after experiment	$\Delta N_{H2} \cdot 10^{-16}$	Experiment No.	$N_{H2} \cdot 10^{-16}$ before experiment	Vapor pressure, mm C_6H_{12}	Vapor pressure, mm C_6H_6	$N_{C_6H_{10}} \cdot 10^{-16}$	$N_{H2} \cdot 10^{-16}$ after experiment	$\Delta N_{H2} \cdot 10^{-16}$
1	7.1	—	—	2.8	7.3	0.2	5	16.4	$2 \cdot 10^{-2}$	—	2.8	15.6	−0.8
2	9.8	—	—	2.8	9.8	0.0	6	15.6	—	$3.1 \cdot 10^{-2}$	—	15.6	0.0
3	17.2	—	—	2.8	16.4	−0.8	7	15.6	—	$3.1 \cdot 10^{-2}$	2.8	13.3	−2.3
4	16.4	$2 \cdot 10^{-2}$	—	—	16.4	0.0	8	13.3	—	—	2.8	12.8	−0.5

For this purpose experiments were carried out which differed from those presented in Table 1 in that a definite pressure of hydrogen was created in the vessel with the platinum film, then vapors of cyclohexane or benzene were introduced,

and only after that were vapors of cyclohexene admitted. The experimental results are summarized in Table 2. The first three experiments showed that if the amount of hydrogen exceeds $9.8 \cdot 10^{16}$ molecules, hydrogenation of cyclohexene predominates, while at smaller amounts dehydrogenation predominates. From experiments Nos. 4 and 5 it follows that cyclohexane is not altered under these conditions and does not affect the transformations of cyclohexene: ΔN_{H2} is the same in experiments Nos. 3 and 5. Benzene is not hydrogenated (see experiment No. 6), but it sharply increases the ratio of the rates of hydrogenation and dehydrogenation of cyclohexene*. This makes it possible to explain the analogous effect in experiment No. 10 of Table 1 by adsorption of benzene, formed in experiment No. 9, on the regions of the film surface where dehydrogenation of cyclohexene occurs. Pumping off the reaction products or specially introduced benzene leads to the usual ratio of the rates of hydrogenation and dehydrogenation, as is seen from experiments Nos. 1–9 of Table 1 and from comparison of the results of experiments Nos. 2 and 3 with No. 8 of Table 2. In all these experiments ΔN_{H2} decreases regularly with increasing N_{H2}.

If the proposed explanation is correct, then with continuous removal of the reaction products more hydrogen should be liberated from cyclohexene,

* Coupled hydrogenation of benzene at the expense of cyclohexene is unlikely in light of the results of work ([3]).

than in the experiments described above. To verify this, two experiments were carried out with one film, with identical amounts of hydrogen in the adsorption vessel, and also with identical rates and durations of cyclohexene admission. In the first experiment, when the entire system was at 20°, the maximum hydrogen pressure was $2 \cdot 10^{-3}$ mm; in the second, the side arm located near the adsorption vessel was cooled with liquid nitrogen. Along with the reaction products, part of the cyclohexene being admitted also condensed in the side arm, but nevertheless the hydrogen pressure exceeded $2 \cdot 10^{-2}$ mm and continued to rise. Consequently, with continuous removal from the platinum film of the benzene formed during the dehydrogenation of cyclohexene, the latter process indeed predominates over hydrogenation.

The foregoing shows that on platinum films at 20°, processes of dehydrogenation and hydrogenation of cyclohexene and cyclohexadiene-1,3 have been observed. At low pressures, dehydrogenation predominates. The accumulation of hydrogen and benzene, which blocks primarily the active centers of dehydrogenation, leads to a decrease in the rate of dehydrogenation and an increase in the rate of hydrogenation. Therefore, with increasing pressure of the unsaturated hydrocarbon, the hydrogen content in the gas phase decreases, and the composition of the reaction products is described ever more accurately by equations (1) and (2), although they do not reflect the transformations studied. To determine whether, alongside them, direct hydrogen transfer also occurs, a special investigation is necessary.

Moscow State University

named after M. V. Lomonosov

Received
9 I 1961

REFERENCES

1. N. D. Zelinskii, *Collected Works*, **3**, Publishing House of the Academy of Sciences of the USSR, 1955.

2. A. A. Balandin, ZhRKhO, **61**, 909 (1929).

3. E. A. Braude, R. P. Linstead, P. W. D. Mitchell, *J. Chem. Soc.*, 1954, 3578.

4. N. A. Shcheglova, M. Ya. Kagan, ZhFKh, **23**, 1083 (1949).

5. *Handb. of Chemistry and Physics*, **37**, 1955–1956.

6. V. M. Gryaznov, V. I. Shimulis, V. D. Yagodovskii, DAN, **132**, 1132 (1960).

7. V. M. Gryaznov, V. I. Shimulis, *Vestn. MGU*, ser. 2, chemistry, No. 5 (1961).

8. V. M. Gryaznov, V. I. Shimulis, *Kinetics and Catalysis*, **2**, No. 4 (1961).

9. V. M. Gryaznov, V. I. Shimulis, T. V. Dilingerova, *Vestn. MGU*, ser. 2, chemistry, No. 6 (1961).

10. V. M. Gryaznov, V. I. Shimulis, *Kinetics and Catalysis*, **2**, No. 5 (1961).

Note: Figure translations are in progress. See original paper for figures.