B. S. GUDKOV, Academician A. A. BALANDIN, E. P. SAVIN

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

B. S. GUDKOV, Academician A. A. BALANDIN, E. P. SAVIN

ISOTOPIC EXCHANGE OF CYCLOBUTANE WITH DEUTERIUM OVER EVAPORATED METALLIC FILMS

A number of studies are known that are devoted to the isotopic exchange of saturated cyclic hydrocarbons with deuterium over various catalysts. The compounds studied include cyclopropane ([1]-[4], [7]), cyclopentane ([4]-[7]), cyclohexane ([4]-[6], [8]-[12]), cycloheptane ([5], [7]), cyclooctane ([5], [7]), and a number of their derivatives ([5], [7], [13], [14]). However, there are no data in the literature on the deuterium exchange of cyclobutane. Only some of its derivatives have been studied, namely 1,1-dimethylcyclobutane ([14]) and ethylcyclobutane ([7], [12]), and the data on them are not systematic. Thus, exchange with ethylcyclobutane was carried out only on Cr_2O_3 gel at 200 and 235° ([7]) and on evaporated nickel at 150°, while exchange with 1,1-dimethylcyclobutane was carried out on a palladium film at 68°. In both cases, the presence of substituents complicates the picture of the distribution of deuterium-exchange products and makes its interpretation difficult. Meanwhile, cyclobutane is an interesting object for investigation, since, while having a structure simpler than that of the higher cyclanes, it is at the same time considerably more stable under catalytic conditions at low temperatures than cyclopropane. In this sense, cyclobutane can serve as a touchstone for testing certain hypotheses concerning the deuterium exchange of cyclic hydrocarbons.

Burel and co-workers ([5]) suggested that, in isotopic exchange, chemisorption of the hydrocarbon takes place with detachment of hydrogen atoms from two neighboring carbon atoms; in order for the exchange to propagate, the carbon-surface bonds must lie in one plane (an eclipsed conformation). In their opinion, it is precisely the absence of eclipsed neighboring bonds that would lie on opposite sides of the ring plane in cyclopentane and cyclohexane (in the "chair" form) that explains the presence of a break in the distribution curve of the deuterium-exchange products after exchange of half the atoms (a peak at $C_5H_5D_5$ and $C_6H_6D_6$, respectively). Already for cycloheptane, which can have, albeit at the cost of some internal strain, eclipsed trans hydrogen atoms, this break is smaller, and for cyclooctane it practically disappears. If this concept is correct, then in the case of cyclobutane, which has an almost planar molecule and in which all neighboring C—H bonds on one side of the ring are eclipsed, the break between $C_4H_4D_4$ and $C_4H_3D_5$ should be clearly expressed.

In Rooney' s work ([14]) it was suggested that deuterium exchange in cyclanes proceeds through the formation of an intermediate π-allylic compound. As a consequence, multiple exchange in cyclobutane should be hindered, since formation of the allylic form would cause considerable strain in its ring.

In our previous studies (^{9})* we obtained experimental indications that, on the surface of Pt, Pd, and Ni, a portion of the cyclohexane molecules, during its exchange with deuterium, is oriented flat, and that on Fe, W, and Mo all cyclohexane molecules have an edgewise orientation. This follows from the fact that, in exchange over Pt, Pd, and Ni with an A1 lattice, the distribution curve of the deuteration products has an intermediate maximum for $C_6H_6D_6$, which was also observed earlier by other authors (^{4,5}), whereas for Fe, W, and Mo with an A2 lattice there is no such maximum. This agrees with the principle of structural correspondence of multiplet theory. From this point of view, a flat arrangement of cyclobutane on Pt, Pd, and Ni is unlikely.

In the present work we studied the deuterium exchange of cyclobutane over evaporated films of Pt, Pd, Ni, W, and Mo at temperatures from 0 to 171°.

Table 1

Distribution of the products of deuterium exchange of cyclobutane

Metal	T_{ra}, °C	Cyclobutane 1	Cyclobutane 2	Cyclobutane 3	Cyclobutane 4	Cyclobutane 5	Cyclobutane 6	Cyclobutane 7	Cyclobutane 8	*n*-Butane 9	*n*-Butane 10	*n*-Butane 11	*n*-Butane 12
Platinum	0	1,000	0,923	0,770	0,498	0,274	0,142	0,058	0,025				
Platinum	70	1,000	0,940	0,856	0,733	0,521	0,318	0,236	0,146				
Platinum	128	1,000	0,745	0,535	0,398	0,190	0,131	0,091	0,053				
Platinum	171	1,000	0,718	0,620	0,410	0,200	0,190	0,164	0,185				
Tungsten	0	–	0,294	0,314	0,338	0,407	0,633	0,840	1,000	0,025	0,034	0,048	0,079
Tungsten	70	0,043	0,027	0,027	0,047	0,068	0,210	0,256	1,000	0,051	0,014	0,040	0,059
Tungsten	105	–	0,050	0,065	0,074	0,121	0,220	0,303	1,000	0,018	0,003	0,006	0,008
Tungsten	160	0,190	0,118	0,135	0,146	0,190	0,310	0,432	1,000				
Molybdenum	34	0,232	0,109	0,096	0,056	0,069	0,232	0,453	1,000				
Molybdenum	126	–	0,081	0,102	0,114	0,152	0,342	0,599	1,000	0,052	0,010	0,018	0,021
Molybdenum	160	0,102	0,088	0,097	0,105	0,105	0,268	0,438	1,000	0,058	0,054	0,111	0,132
Palladium	0	1,000	0,155	0,078	0,043	0,024	0,015	0,011	0,008				
Palladium	34	1,000	0,674	0,372	0,115	0,042	0,024	0,023	0,027	0,024	0,027	0,027	0,043
Palladium	60	1,000	0,370	0,156	0,051	0,020	0,017	0,019	0,023	0,020	0,029	0,033	0,068
Nickel	42	1,000	0,346	0,234	0,136	0,051	0,039	0,034	0,046	0,027	0,061	0,078	0,251
Nickel	155	0,955	0,580	0,380	0,196	0,076	0,062	0,081	0,145	0,175	0,434	0,675	1,000

The experimental procedure and the method of analysis did not differ from

---

* See also the paper submitted to the journal *Izv. AN SSSR, Chemical Series.*

Fig. 1. Change in the form of the distribution curve with time during exchange over Pt at 128° (I), over W at 70° (II), and over Pd at 34° (III). a –5 min, b –15 min, c –30 min, d –60 min

Figure 1: Fig. 1. Change in the form of the distribution curve with time during exchange over Pt at 128° (I), over W at 70° (II), and over Pd at 34° (III). a –5 min, b –15 min, c –30 min, d –60 min

those we used previously (^{9}). The ionizing voltage of the mass spectrometer was 20 V. Cyclobutane was obtained by reduction of cyclobutanol with hydrazine hydrate (^{15}) and subjected to low-temperature distillation, after which mass-spectrometric and gas-chromatographic analysis showed the absence of any appreciable impurities in the main product. Deuterium from a cylinder (content D_2 98%) was purified by passage through a diffusion nickel lamp. The ratio of the reactants was $C_4H_8 : D_2 \approx 1 : 30$ at a total pressure of 27 mm Hg.

The results of the experiments are presented in Table 1. The amounts of the individual deuterium-exchange products are given in relative units. The values in the first eight columns correspond mainly to different degrees of exchange of cyclobutane (a minor contribution is made by deuterated *n*-butane). The subsequent four columns refer to products of hydrogenolysis of cyclobutane with ring opening and formation of *n*-butane, accompanied by its exchange. In the case of Pt, ring cleavage does not occur at all, and for the other metals (with the exception of Ni) it does not seriously affect the distribution pattern. This indicates the relative stability of cyclobutane toward hydrogenolysis under the conditions of our experiments.

For none of the metals was a discontinuity observed in going from $C_4H_4D_4$ to $C_4H_3D_5$, and the peak corresponding to exchange of half of the hydrogen atoms is completely absent. An increase in temperature, as is seen from Table 1, has little effect on the character of the distribution, causing only an increase (Mo, Pd, Ni) or a decrease (W) in the degree of hydrogenolysis of cyclobutane relative to isotopic exchange. The table gives values corresponding to such an extent of exchange at which the consumption of cyclobutane and its hydrogenolysis do not yet introduce serious distortions into the distribution picture (not more than 20%, in the case of W up to 30%). Figure 1 shows the course of the change in the distribution pattern with time for Pt, Pd, and W.

Fig. 1. Change in the form of the distribution curve with time during exchange over Pt at 128° (*I*), over W at 70° (*II*), and over Pd at 34° (*III*). *a* –5 min, *b* –15 min, *c* –30 min, *d* –60 min.

If in the case of Pt and Pd the general form of the curve changes little, then in the case of W, where a gradual transition of deuterium to highly deuterated *n*-butane occurs, this change is very substantial.

Analysis of Table 1 leads to the conclusion that our data do not support the view of Barel discussed above. Evidently, the absence of adjacent eclipsed C–

H bonds located on opposite sides of the ring does not prevent the spread of exchange to the other side. Otherwise, during exchange of the hydrogen atoms of cyclobutane, a maximum at $C_4H_4D_4$ or a break between $C_4H_4D_4$ and $C_4H_3D_5$ should have been observed. Rooney' s views on the role of the allylic grouping (see above) are likewise not confirmed, since in our experiments multiple exchange on all the catalysts studied, except Pd, plays a very important role. The fact that for cyclobutane the maximum on the distribution curve is equally absent when exchange is carried out both over metals with a face-centered cubic lattice (Pt, Pd, Ni) and over metals with a body-centered lattice (W, Mo) may be regarded as confirmation of the structural views of the multiplet theory. Indeed, between cyclobutane and the indicated metals there is no structural correspondence of the kind that exists between cyclohexane and Pt, Pd, and Ni (9).

On the basis of the multiplet theory, the absence of a peak at $C_4H_4D_4$ and the formation of highly deuterated products can be explained by an edge orientation of the cyclobutane ring upon adsorption on the surface (doublet scheme), analogous to the edge orientation of cyclohexane (16).

It is interesting to note that the rate of hydrogenolysis of cyclobutane relative to the rate of deuterium exchange increases in the series Pt, Pd, Ni (cf. Table 1).

This may be connected with the fact that the C–C distance in cyclobutane (1.568 Å) (^17) corresponds most closely to the distances between the troughs of the (111) plane of the Pt crystal lattice (1.603 Å, cf. Fig. 196 in (^16)). In the case of Ni, the distance between the troughs (1.438 Å) is such that it produces a certain strain in the cyclobutane ring, which may lead to its opening.

The decrease, occurring in the reaction over W, in the degree of hydrogenolysis of cyclobutane with increasing temperature, as compared with isotope exchange, is consistent with the previously observed anomalies in the behavior of this metal in catalytic reactions.

Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
11 IX 1964

CITED LITERATURE

1. G. C. Bond, J. Turkevich, *Trans. Farad. Soc.*, **50**, 1335 (1954).

2. G. Bond, D. Addy, in: *Collected Papers on Catalysis. Proceedings of the First International Congress*, IL, 1960, p. 55; G. C. Bond, J. Addy, *Adv. in Catal.*, **9**, 44 (1957).

3. J. Addy, G. C. Bond, *Trans. Farad. Soc.*, **53**, 368, 383, 388 (1957).

4. J. R. Anderson, C. Kemball, *Proc. Roy. Soc.*, A **226**, 472 (1954).

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

6. R. L. Burwell, R. H. Tuxworth, *J. Phys. Chem.*, **60**, 1043 (1956).

7. C. T. H. Stoddart, G. Pass, R. L. Burwell, *J. Am. Chem. Soc.*, **82**, 6272, 6284 (1960).

8. T. Hayakawa, T. Sugiura, *Bull. Chem. Soc. Japan*, **31**, 180, 186, 190 (1958).

9. A. A. Balandin, B. S. Gudkov, R. M. Fedorovich, *DAN*, **155**, 626 (1964).

10. Kh. M. Minachev, E. G. Vakk, R. V. Dmitriev, *Izv. AN SSSR, OKhN*, 1962, 1086.

11. Kh. M. Minachev, E. G. Vakk et al., *Izv. AN SSSR, Ser. Khim.*, 1964, 421.

12. H. C. Rowlinson, R. L. Burwell, R. H. Tuxworth, *J. Phys. Chem.*, **59**, 225 (1955).

13. F. G. Gault, J. J. Rooney, C. Kemball, *J. Catalysis*, **1**, 255 (1962).

14. J. J. Rooney, *J. Catalysis*, **2**, 53 (1963).

15. J. D. Roberts, C. W. Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949).

16. A. A. Balandin, *Multiplet Theory of Catalysis*, Part 1, Moscow, 1963.

17. *Tables of Interatomic Distances*, Chem. Soc., London, 1958.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.