ACTIVE CARRIERS DURING HYDROGENATION

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Catalytic hydrogenation requires activation on the surface of the catalyst of both the hydrogen and of the hydrogenated compound. Naturally, the most favorable conditions for activation of the separate components may not coincide and an increase in temperature almost always changes not only the speed of the primary reaction, but also the relative concentrations of the reacting substances on the catalyst surface. As a result, there is observed a negative temperature coefficient above 40° [1] when a majority of organic compounds are hydrogenated in the presence of elementary nickel catalyst. By activating, or inactivating, the catalyst, it is possible to increase or to decrease the activation of one of the reacting components. Thus, for example, when Pt, Pd or Rh is deposited upon nickel catalyst, the hydrogen is almost always principally activated, whereas Os, Ru and Re actually lower the activity of nickel catalyst. At room temperature osmium black displays activity upon hydrogenation of the double bond, the carbonyl group and the nitro group [2], during which time the hydrogenation proceeds stepwise. Under these conditions, acetylenic hydrocarbons do not fully hydrogenate, which is explained by the competition between the hydrogen and the acetylene group on one and the same sections of the catalyst. During hydrogenation on Pt, Pd or Ni, both the adsorbed and the dissolved hydrogen take part in reaction. To a lesser extent the question of activation of the unsaturated component during reaction has been studied. In this case it may be expected that the structural correspondence between catalyst and reacting molecule will be of primary importance. An assumption has been made that superficially completely inactive osmium and ruthenium blacks actually activate the double bond, and active hydrogen is lacking only on their surface. Following deposition on their surfaces of palladium or of platinum, which activate hydrogen particularly well, the potential possibilities of such "active carriers" should be manifested, and it should be possible to obtain highly active catalysts. This assumption was fully confirmed, using the hydrogenation of dimethylacetylenylcarbinol.

EXPERIMENTAL

(With the assistance of N. Sinaiskaya and M. Zakharova)

The hydrogenation was studied in 96% ethanol solution under conditions described earlier [3]. For catalysts were used: Pt, deposited on $BaSO_4$, or on $BaSO_4$ coated first with Os, and also by Pd on $BaSO_4$ coated with ruthenium. The active carriers were prepared according to the method of N. D. Zelinsky [4], calculated in such amount as to obtain a 20% Os or Ru content on $BaSO_4$. The "active carriers" were dried at room temperature in a dessicator over H_2SO_4. Their characteristic activity was examined by hydrogenation of nitro benzene and was found to be equal to zero. Part of the Os–$BaSO_4$ and Ru–$BaSO_4$ was reduced at 200° for 4 hours and subsequently remained inactive. A weighed portion of "active carrier", equal to 2 g, was transferred to a flask with the aid of 15 ml of alcohol; there was also introduced, by a pipet, a defined volume of chlorplatinate or of palladium chloride solution. The flask was shaken for 30 minutes, for better adsorption of the promoter, and the catalyst was further saturated with hydrogen for 30 minutes at 25°. After saturation, there was placed in the flask a defined weight of dimethylacetylenylcarbinol and 10 ml of alcohol was added. The system was washed rapidly with hydrogen, the motor switched on and readings on absorbed hydrogen started.

Hydrogenation of Dimethylacetylenylcarbinol on Catalysts Pt–$BaSO_4$ and Pd–$BaSO_4$. It was found that the hydrogenation rates of the double and of the triple bond on Pt and Pd deposited on $BaSO_4$ differed. In Fig. 1 is represented a series of kinetic curves for the hydrogenation of dimethylacetylenylcarbinol on Pt–$BaSO_4$ catalyst. One peculiarity is characteristic for all curves – the reaction rate remains almost stationary up to the absorption of approximately 70-75% of the calculated volume of hydrogen and then increases sharply.

It may be assumed that on the first horizontal segment, linkage of one hydrogen molecule to the triple bond occurs, and simultaneously partial hydrogenation of the ethylene derivative produced starts. As soon as hydrogenation of the triple bond is terminated, the double bond starts to hydrogenate with much greater speed. To examine this assumption, the experiments were interrupted at the moment when the increase in reaction rate started. The products of incomplete hydrogenation were poured off rapidly from the catalyst and tested for the presence of hydrogen at the triple bond by the use of ammoniacal silver nitrate; in all cases the absence of the acetylenic alcohol was established.

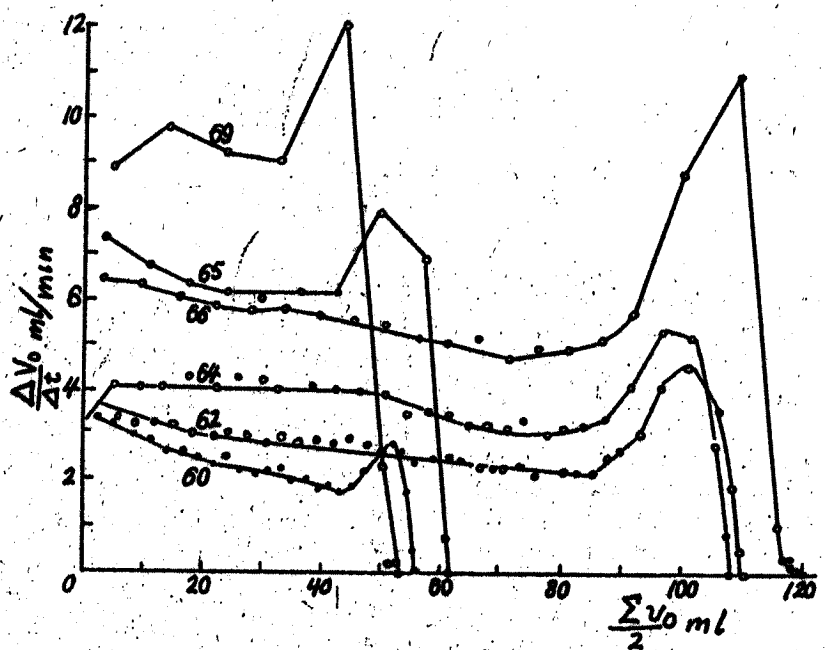

Fig. 1. Hydrogenation of Dimethylacetylenylcarbinol on Pt–$BaSO_4$ Catalyst. ($BaSO_4$ 0.2 g, ethyl alcohol 25 ml).

Expt. No.	Quantity of Pt (g)	Temperature	Quantity of Carbinol (ml)
60	0.00103	25°	0.12
62	0.00103	25	0.24
64	0.00103	40	0.24
65	0.00206	25	0.13
66	0.00206	25	0.26
69	0.00206	40	0.12

It is known that Pt dissolves very little hydrogen and, furthermore, under our conditions, the Pt atoms either form very fine crystals or penetrate into the incomplete lattice work of the carrier; thus adsorbed hydrogen plays the principal role in hydrogenation. Compounds with a triple bond adsorb very well on the surface of the platinum metal group, and, in addition, they are activated on the centers, that are similar to the centers which activate the hydrogen. [1]. As a result of this competition, the speed of hydrogenation of the triple bond on platinum catalysts is usually smaller than the speed of hydrogenation of the double bond. In the absence of compounds with a triple bond, the hydrogen concentration on the surface increases. In complete accordance with this view, as the curves of Fig. 1 indicate, the hydrogenation speed of the triple bond decreases with the dimethylacetylenylcarbinol increase in concentration and the hydrogenation speed of the double bond increases.

For characterization of curves of a similar type, we are introducing the value, a, representing the relation between the maximum speed of hydrogenation to the average speed of hydrogenation of the triple bond (the first segment of the curve). The value, a, as experiments indicate, depends very little upon the activity of the catalyst, upon the quantity of Pt deposited upon $BaSO_4$, or upon the temperature. Thus, in a whole series of experiments with 0.12 ml of dimethylacetylenylcarbinol, upon a change in quantity of Pt from 0.00103 to 0.00412 g, and a temperature from 25 to 40°, the relation of speeds a changed only from 1.1 to 1.3, i.e., within the range of experimental error. Contrariwise, the value a, is very sensitive to concentration change, and under the same conditions, with 0.24 ml of dimethylacetylenylcarbinol, fluctuated from 1.7 to 2.2.

It should be noted that with an increase in temperature the hydrogenation speeds of the triple and the double bond increase, but the former rises more rapidly and the relation of the speed a decreases somewhat. This phenomenon is quite understandable if one assumes that, with temperature rise under the conditions involved, the speed of the primary reaction increases and general adsorption decreases.

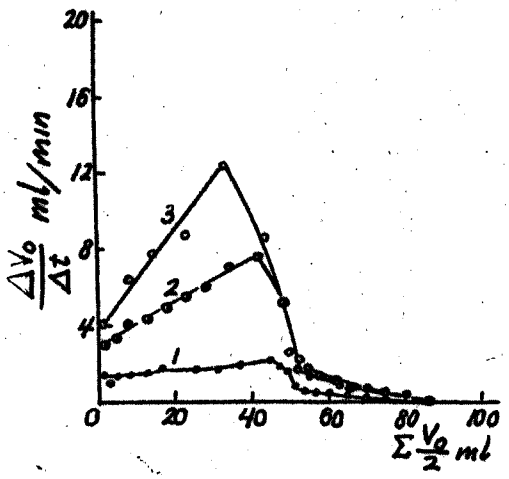

Fig. 2. Hydrogenation of Dimethylacetylenylcarbinol on catalyst Pd–$BaSO_4$. ($BaSO_4$ 0.2 g., Pd 0.00012 g, ethyl alcohol 25 ml).

Expt. No.	Temperature
1	1°
2	25
3	40

TABLE 1

Added Pt (g)	Carbinol taken (ml)	Temperature	a average
0.00051	0.12	25°	4.20
	0.24	25	4.70
	0.12	40	3.85
0.00103	0.12	25	2.63
	0.12	40	2.50
	0.24	40	4.30
0.00206	0.12	25	1.95
	0.24	25	3.00

In Fig.2 is represented a series of curves on another catalyst, Pd–$BaSO_4$. In this case the correlation of speeds is entirely different; the reaction speed in the first half of the process is considerably greater than in the second and consequently the triple bond hydrogenates more rapidly than the double bond. Selectivity of the catalyst in this case is considerably greater, and the break in the speed, corresponding to a loss of a triple bond in the compound, is observed after absorption of 55-68% of the calculated quantity of hydrogen (reaction with ammoniacal $AgNO_3$). A similar course of the curves in the presence of Pd, which is similar in lattice structure to that of Pt, can be related only to the participation of dissolved hydrogen in the reaction. It is known that Pd dissolves hydrogen readily and that this hydrogen takes part in the reaction, as we have shown earlier [3]. In this instance the hydrogen and the acetylene derivative activation are basically related to the different surface sections, or more correctly, with the mass of the catalyst. The gradual increase in speed during the first half of the process can be related to the increased role of adsorbed hydrogen by the rate of concentration decrease of the compound with the triple bond. Thus, in the case of palladium catalyst, it is impossible to limit oneself to examination of the role of dissolved hydrogen only. It is necessary to take into account the gradual increase in role of the adsorbed hydrogen. The variable correlation of hydrogenation speeds of the triple and double bonds in the presence of Pt and Pd on $BaSO_4$ made it of particular interest to study the effect of Os and Ru as a coater from the point of view of clarifying this correlation.

As has already been mentioned, Os and Ru on $BaSO_4$ were found to be entirely inactive in the hydrogenation reaction. Both metals have the hexagonal lattice with parameters: Os a 2.7244 Å, with 4.3044 Å, Ru a 2.695 Å, with 4.273 Å, and can, from structural considerations, at low temperature, only result in activation of the double bond by a given amount of hydrogen and not the triple bond.

Hydrogenation of Dimethylacetylenylcarbinol on catalyst Pt–[Os–$BaSO_4$]. A series of curves is represented in Fig.8, which were obtained in the presence of Os. The shape of the curve remains the same under all conditions, and is similar to the curves obtained in the absence of Os. However, the hydrogenation speed of the triple bond is almost unchanged and the hydrogenation speed of the double bond increases sharply. As a result, the value a, increases also. Thus, the presence of Os can be considered to be catalyzing only in relation to the second part of the process, i.e., to the hydrogenation of dimethylvinylcarbinol. Upon increase in concentration of the dimethylacetylenylcarbinol, the hydrogenation speed of the triple bond decreases and the hydrogenation speed of the double bond increases (curves for Experiments 5 and 6, 9 and 10, 30 and 31, 16 and 17).

The deductions made become more graphic when the average values for "a" (Table 1) are calculated.

As can be seen from Fig.3 and from the data of Table 1 during the small steps in the filling of the platinum surface, an acceleration in double bond hydrogenation is noticed.

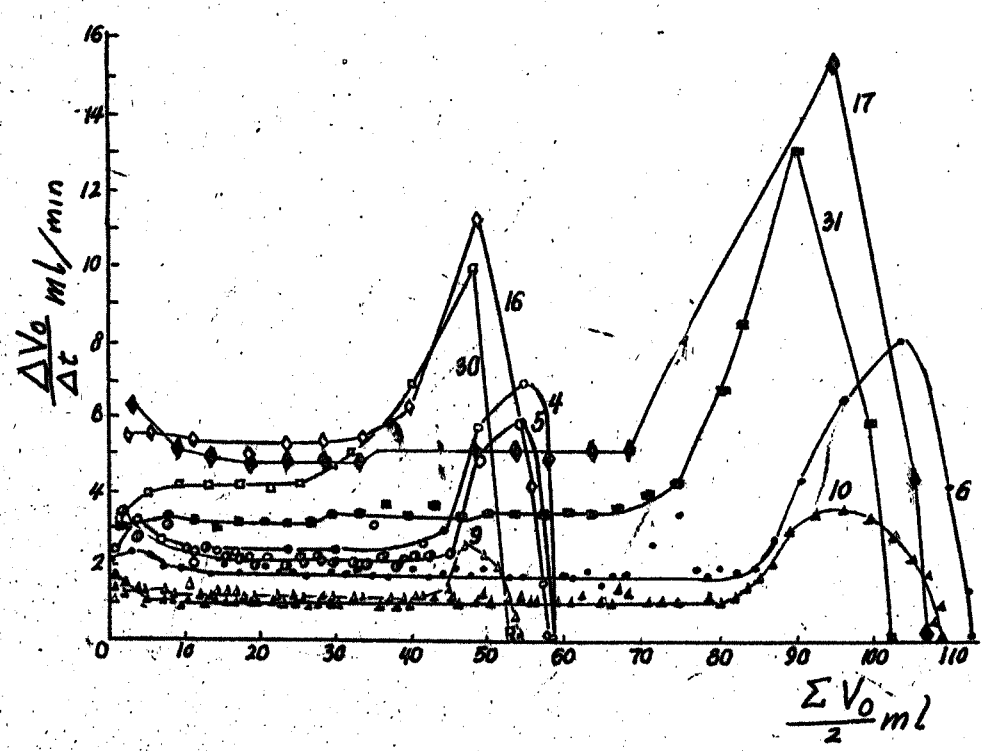

Fig. 3. Hydrogenation of dimethylacetylenylcarbinol on catalyst Pt–[Os–$BaSO_4$]. (Os–$BaSO_4$ 0.2 g, ethyl alcohol 25 ml).

Expt. No.	Pt Quantity (g)	Temperature	Carbinol quantity (ml)
4	0.00103	25°	0.12
5	0.00103	25	0.12
6	0.00103	25	0.24
9	0.00051	25	0.12
10	0.00051	25	0.24
30	0.00103	40	0.12
31	0.00103	40	0.24
16	0.00206	25	0.12
17	0.00206	25	0.24

For a given quantity of Pt during the greatest changes in activity of the catalyst, the correlation of the hydrogenation speeds, a, is almost unchanged. The same regularities were found by the author upon subsequent filling up of the Os–$BaSO_4$ surface by platinum, beginning with from 0.00021 to 0.00165 g of Pt for 0.2 g of "active carrier". Pt on Os–$BaSO_4$ was found to be a very stable catalyst and it is possible to conduct more than 10 experiments on the one sample without noticeable lowering of the activity.

Similar series of experiments were carried out with Pt, deposited on Os–$BaSO_4$, previously reduced at 200°. It is necessary to note that the catalyst in this case is even more stable and active. A very interesting phenomenon was observed after prolonged work with one and the same weighed sample of reduced catalyst: the activity of the catalyst decreased from experiment to experiment and the relation of the hydrogenation speeds of the double and the triple bonds, a, increased. This experimental result can be explained by the fact that the Pt atoms are able in time to penetrate deeply into the crystalline lattice of the Os–$BaSO_4$ carrier, as the result of which "a" increases.

Hydrogenation of dimethylacetylenylcarbinol on catalyst Pd–[Ru–$BaSO_4$]. The kinetic hydrogenation curves are represented in Figs. 4, 5, 6. The triple bond hydrogenates in this case considerably more rapidly than the double bond. Comparative data on hydrogenation in the presence of, and in the absence of, Ru are given in Table 2 for the two series of experiments.

TABLE 2

Series and catalyst	Expt. No.	Temp.	Carbinol t'aken (ml)	Maximum speed (ml/min.)	K for hydrogenation of double bond	Duration of hydrogenation (in min.)	
						of the triple bond	of the double bond
VIII $BaSO_4$ + 0.00036 g Pd	29	25°	0.2	26.5	0.87	2	22
	30	40	0.2	38.7	1.60	1	14
IX Ru–$BaSO_4$ + 0.00036 g Pd	32	25	0.2	30.0	2.15	2	7
	33	25	0.2	30.5	1.88	2	7
	35	40	0.2	48.3	3.73	1	6
	36	40	0.4	51.1	4.01	2	7
	37	40	0.6	50.7	4.01	3	10
	34	25	0.2	28.0	–	2	8
	31	1	0.2	10.0	0.44	5	27
	38	25	0.2	25.5	1.88	2	9
	39	25	0.4	26.7	1.80	4	13
After 72 hours of standing for the catalyst	40	1	0.4	7.4	0.28	15	45

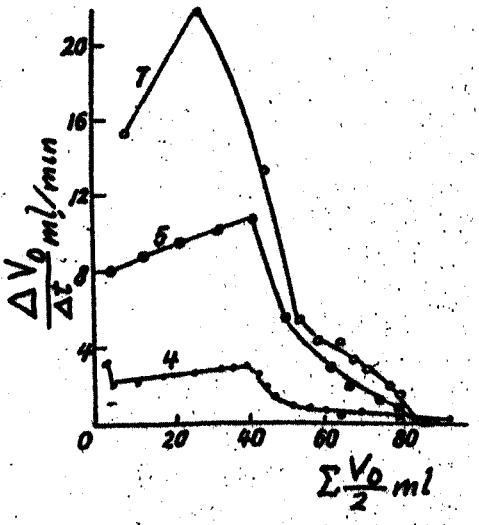

Fig. 4. Hydrogenation of dimethylacetylenylcarbinol on catalyst Pd–[Ru–$BaSO_4$]. (Ru–$BaSO_4$ 0.2 g Pd 0.00012 g, ethyl alcohol 25 ml).

Expt. No.	Temperature
4	1°
5	25
7	40

TABLE 3

Temp. interval	Catalyst			
	Pd–$BaSO_4$		Pd–[Ru–$BaSO_4$]	
	E of triple bond hydrogenation (cal/mol)	E of double bond hydrogenation (cal/mol)	E of triple bond hydrogenation (cal/mol)	E of double bond hydrogenation (cal/mol)
1-25°	8-9000	7-8000	7-8000	8-9000
25-40	4-5000	6-7000	5-6000	6-7000

As can be seen from the data of Table 2 and the curves of the graphs, the average speed of hydrogenation in the presence of Ru, at all temperatures is considerably higher. However, the hydrogenation time of the triple bond, in the presence of Ru, is the same as without it, while the hydrogenation time of the double bond in the presence of Ru decreases from 22 to 7 minutes, i.e., more than threefold. The relation of hydrogenation speed $\frac{K(Ru)}{K(\text{without Ru})}$ constitutes: at 25°, 2.3; at 40°, 2.33; of maximum speed at 25°, 1.18; at 40°, 1.25. In all other series of experiments the hydrogenation speed of the double bond also increases more rapidly than the hydrogenation speed of the triple bond. The presence of Ru starts to become noticeable at elevated temperature (40°), evidently, as the result, the activation of the unsaturated bonds over Ru is hampered by low temperature. As can be seen from the data of Table 1 and of Fig. 6, the maximum hydrogenation speed is almost independent of the concentration of dimethylacetylenylcarbinol in solution. The catalyst Pd–[Ru–$BaSO_4$] is very stable and all experiments of the series were carried out with one catalyst. It should be noted that, with an increase in the quantity of palladium, at a constant quantity of Ru, the effect of the latter begins to weaken and the catalyst approaches that of the catalyst Pd–$BaSO_4$.

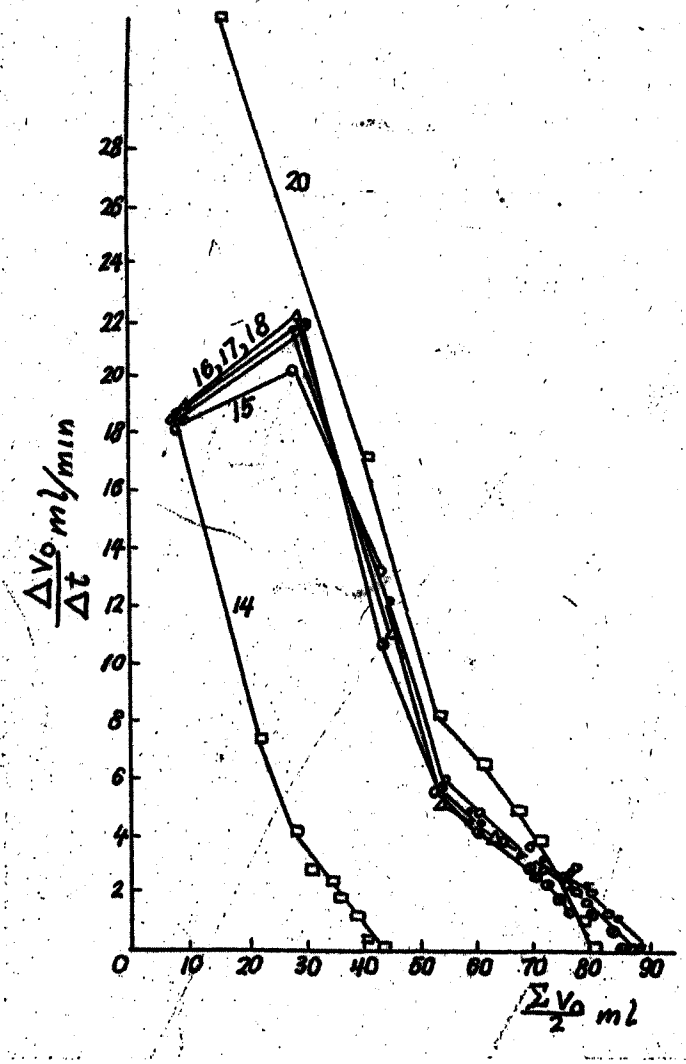

Fig. 5. Hydrogenation of dimethylacetylenylcarbinol with catalyst Pd–[Ru–$BaSO_4$]. (Pd 0.00024 g).

Expt. No.	Temperature	Carbinol quantity (ml)
14	25°	0.1
15,16,17,18	25	0.2
20	40	0.2

Upon deposition of 0.00048 g of Pd, the difference in the properties of the catalysts with Ru becomes evident only at high temperature. The activation energies for the hydrogenation of the triple bond and of the double bond are found on the basis of 13 series of experiments to be variable for catalysts with and without Ru (Table 3).

The activation energy for the triple bond and for the double bond hydrogenation is considerably higher in the temperature interval 1-25° than in the interval 25-40° as can be seen from the data of Table 3.

At the elevated temperatures, the ability of the unsaturated compound to extract dissolved hydrogen from the catalyst increases and along with it the quantity of hydrogen adsorbed on the surface is decreased. The conjugation of the two factors augments the role of dissolved hydrogen, of which diffusion there is naturally a small temperature coefficient. In almost all cases the activation energy for hydrogenation of the triple bond was found to be lower than that for the double bond.

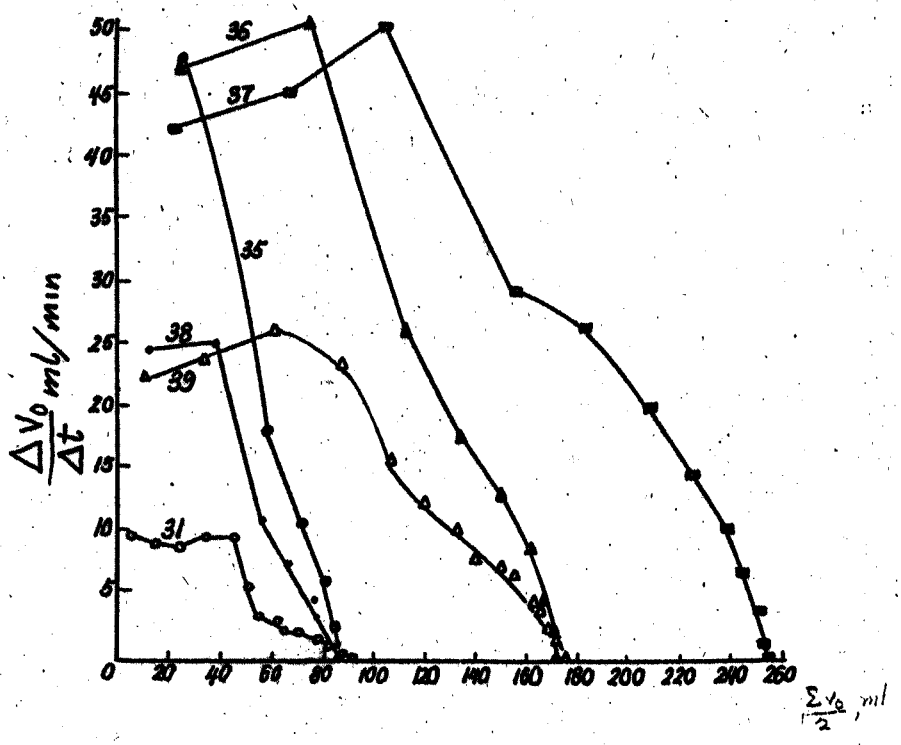

Fig. 6. Hydrogenation of dimethylacetylenylcarbinol with Pd – [Ru – $BaSO_4$]. (Pd 0.00036 g).

Expt. No.	Temperature	Carbinol quantity (ml)
31	1°	0.2
38	25	0.2
39	25	0.4
35	40	0.2
36	40	0.4
37	40	0.6

SUMMARY

The results obtained by the author indicate the necessity for examining separately the effect of carrier upon the behavior of hydrogen and the hydrogenated compound in hydrogenation reactions. In the case of hydrogenation of dimethylacetylenylcarbinol, Os and Ru, on $BaSO_4$, were found to be the carriers which first of all activate the double bond, regardless of the fact that there is an entirely opposite correlation for hydrogenation speeds for the double and the triple bond, which is conditioned by variable percentage participation in reaction of the dissolved and the adsorbed hydrogen upon Pt and Pd. The different effects of substituents on the hydrogenation speed upon Pt and Pd were also demonstrated by B. A. Kazansky and G. T. Tatevosyan [5]. In the case examined, the structural correlation between the molecule and the catalyst enters into the foreground.

The problem of structural correlation acquires now particular actuality in the light of discussion on the "theory of resonance" and it seems somewhat strange that some authors recently have been prepared to reject entirely this principle in organic catalysis. It is inevitable, no doubt, to reject certain complex elements of symmetry, postulated by the multiple theory and hardly realizable from the point of view of no less obligatory energy correlation.

In the case given, the problem of energy correlation is presented only in the sense of a distinction in the

role of adsorbed and dissolved hydrogen. Potentiometric measurements demonstrate that the catalyst potential falls rapidly when compounds with a triple bond are hydrogenated on Pt, regardless of how small the speed of reaction is; during the transition to double bond hydrogenation, the reaction rate and the potential both increase sharply at the same time.

The increase in the amount of hydrogen at the surface with the increase in reaction rate can only be connected with the fact that in the presence of acetylene derivatives, hydrogen desorbs from the surface and passes off into the gaseous state.

The quantity of hydrogen which can be diluted in 0.00048 g of Pd (maximum quantity) is quite insufficient for hydrogenation and evidently there occurs incessantly in the course of the reaction, replenishment of the dissolved hydrogen. Hydrogen on Os and Ru activates only with great difficulty and predominantly at increased temperatures. In this manner some decrease of $\underline{a}$ with increase in temperature can be explained.

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