POLAROGRAPHIC INVESTIGATION OF THE HYDROGENATION PROCESS. I.

A. L. Markman

An examination of the methods used by various authors for studying the behavior of unsaturated compounds in the course of catalytic hydrogenation shows that we can subdivide them into two groups. To the first group belong methods based on the establishment of the velocities of hydrogenation of individual unsaturated compounds and on the comparison of these velocities for a series of chemically related compounds.

In the majority of cases the velocity of saturation of unsaturated compounds is measured by the volume of hydrogen which combines in unit time, or by the time required for saturation of a specified quantity of substance expressed as moles, or by the time required for addition of a specified volume of hydrogen to a given quantity of the compound, or, finally, the velocity of saturation is measured from the rate of change of some physical constant of the substance, such as the refractive index, the rotatory power, etc..

A number of authors [1-10] have employed the technique of comparing the velocities of saturation of pure compounds to draw conclusions about the effect of the structure of the molecules on the activity of the multiple bond in the process of catalytic hydrogenation. Other authors [11, 12], by hydrogenating mixtures of pure unsaturated compounds with one and the same standard substance, have compared the so-obtained partition coefficients of hydrogen and have established the effect of structural peculiarities of molecules on the reactivity of the double bond.

It has been found, however, that comparison of the rates of saturation of pure compounds, or determination of the coefficients of distribution of hydrogen between pure unsaturated compounds and the standard substance, do not permit us to draw conclusions about the behavior of these unsaturated compounds in mixtures.

The second group of methods of study of the behavior of unsaturated compounds during the hydrogenation process includes the methods of joint hydrogenation of two competing substances, of hydrogenation of binary mixtures with the aim of direct establishment of the order of hydrogenation of the components of the mixture. We must bear the following facts in mind: 1) In the vast majority of cases the experiments were run with small amounts of material (1/200 to 1/100 mole); 2) if the starting mixture contains two components, then the saturation process will lead to at least two hydrogenation products so that the binary mixture is changed into a quaternary mixture; 3) the quantitative separation of compounds, especially when they are similar in functional character, is extraordinarily difficult and in the majority of cases impossible. In order to be able to follow the whole course of the process, it would be desirable to withdraw small samples of reaction mixture at definite intervals of time and to analyze them. But if, say, one-tenth of the mixture is to be withdrawn each time, this would correspond to 1/2000 to 1/1000 mole. It would be a very difficult problem to separate such an amount into the four components for the purpose of establishing the content of each in the mixture. Very rarely, therefore, is the attempt made to effect direct analysis of a mixture at different stages of hydrogenation, and even as a rule for the purpose of evaluating the course of the process of saturation of binary mixtures, recourse is had to indirect methods. The most important of the indirect methods is that developed by S. V. Lebedev [13] which is based on the study of hydrogenation curves.

Such a method, however, does not permit the study of intermediate processes, i.e. with a not strictly maintained selectivity; in the course of the process one component of the mixture is preferentially saturated; at the same time the other component undergoes saturation although at a much lower velocity. The degree of selectivity of the process may vary widely and the hydrogenation curves do not permit us to determine the degree of selectivity.

Other workers apart from S. V. Lebedev who studied the course of hydrogenation of binary mixtures of diolefinic and acetylenic compounds on the basis of the character of the hydrogenation curves were Dupont [14], Armstrong and Hilditch [15] and Yu. S. Zalkind [16].

The marked inadequacy of the information supplied by the hydrogenation curves prompted the first investigators of problems of selectivity of hydrogenation to resort to analysis of the mixtures, using the method of interrupted hydrogenation. This method consists essentially in interrupting the hydrogenation of an equimolecular mixture of two unsaturated compounds when 50% of the theoretical amount of hydrogen has been absorbed and

and then analyzing the mixture as a whole; on the basis of the results of this analysis, conclusions are drawn about the presence or absence of selectivity and about the degree of selectivity of the process.

Of the numerous authors who utilized the method of interrupted hydrogenation, we may mention Vavon [17], Bourguel [18], Yu. S. Zalkind [16, 19], B. A. Kazansky [20] and M. I. Ushakov [9].

Different authors used different methods of analysis of the reaction mixture [21]. In all cases the procedure is quite complicated; the main defect of the method is that it characterizes the state of the process not throughout its entire course, but only at one determined moment.

It is therefore natural to search for a method which would permit the course of the process to be followed at any rate at a few points. The obvious plan is to effect direct or indirect analysis of samples withdrawn from the reaction mixture at intervals throughout the process.

Many attempts to develop a procedure along these lines have been made. We may refer to the work of Vavon [22] who followed the course of hydrogenation of limonene and carvone by withdrawing samples from the reaction mixture at intervals and measuring the angle of rotation of the plane of polarization of light.

In the study of the process of hydrogenation of fats with the objective of establishing its selectivity, Kaufmann [23] and later Zinovyev [24] successfully applied the method of determination of the iodine and thiocyanogen numbers.

V. V. Ipatyev [25] hydrogenated a mixture of allyl alcohol and oleic acid and withdrew samples over definite intervals of time; he determined the amount of stearic acid formed by precipitation with magnesium acetate and the total amount of unsaturated compounds remaining in solution from the amount of iodine chloride absorbed by them. A slightly modified procedure was employed by I. F. Bogdanov and E. L. Bashkirova [26].

Performance of an experiment in the apparatus used in the above-cited investigations [24, 26] necessitated relatively large amounts of unsaturated compounds, in addition to which the procedure for analysis of the mixtures was rather complicated. We therefore reached the following conclusions:

1. Study of the course of the hydrogenation of binary mixtures from the saturation curves (S. V. Lebedev) only gives an approximate conception of the character of the process.

2. The method of interrupted hydrogenation does not give an idea of the state of the process throughout its entire course, so that its value is seriously limited.

3. The method of withdrawal of a series of samples in the course of the process is the most interesting and informative in the sense that it permits study of the kinetics of the process. Up to now, however, the proposed methods of analysis of mixtures have been laborious, only applicable to a limited number of materials, and frequently required large amounts of substance.

In seeking for an analytical method of adequate sensitivity and accuracy, speedy and easy in use, enabling operation with very small quantities of substance, and applicable to a fairly wide range of chemical compounds, we decided on the polarographic method.

In the conditions of the investigation we were faced with the following problem: Knowing that two given unsaturated compounds are present in the mixture to be hydrogenated, and knowing also the amount of hydrogen consumed up to the instant of withdrawal of the sample from the vessel, it is desired to determine polarographically how much of each unsaturated compound is left in solution, assuming that the respective saturated compounds do not give polarograms and that their presence does not affect the polarographic behavior of the unsaturated compounds.

This problem can be solved in two ways, depending upon whether both or only one of the unsaturated components of the mixture give polarograms.

In the event that both components of the mixture give definite and separate polarographic waves, the problem is solved by plotting polarograms at different stages of hydrogenation, by measurement of the height of each wave and, insofar as the proportionality coefficient between the diffusion current and the concentration is known, by calculation of the concentration of each component in the solution. In the course of the hydrogenation reaction, either the heights of the waves of both components will gradually decrease but the change will differ for each component in dependence on the degree of selectivity of the process or both waves will decrease to identical extents at the same time (non-selective process) or the heights will decrease simultaneously, but at different rates (one more quickly than the other—not strictly selective process), or at first only the height of one of the waves will decline and its disappearance will be followed by the start of decline of the other wave (strictly selective process).

In Figure 1 are shown curves obtained by polarographic determination of a series of specimens withdrawn during the hydrogenation of a mixture of maleic and fumaric acids; on these curves the wave at a more positive value of the potential relates to maleic acid; that at a more negative value to fumaric acid. The half-wave potential of maleic acid differs from that of fumaric acid by 0.2 V, which allows of clear demarcation of one wave from the other. Measurements of the height of the waves on the curves gave us the values set forth in Table 1.

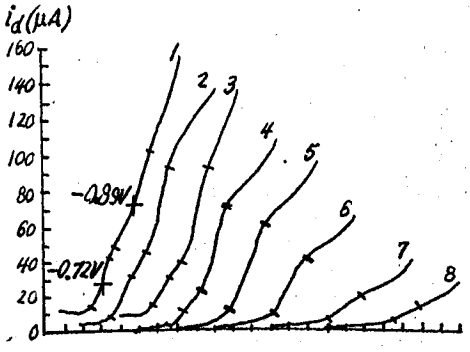

Fig. 1. Polarograms of mixtures of maleic and fumaric acids $\eta = 1/10$. Explanation in text and Table 1.

In the starting solution (specimen no. 1, Table 1) the concentrations of maleic and fumaric acid were taken as equal to:

$$C_m = C_f = 250 \cdot 10^{-5} \text{ mol/ liter.}$$

We see from the data of Table 1 that maleic acid is preferentially hydrogenated in comparison with fumaric acid; the selectivity, however, is not strict since at the instant of complete disappearance of maleic acid, the fumaric acid has been partly (only to the extent of 17%) hydrogenated.

In some cases it is useful to obtain information about the concentration of the substance which is being analyzed by applying the so-called method of addition of a standard solution, which ensures greater accuracy of determination, although a longer period is then required for the determination. In the present investigation we resorted to this method in many cases.

When only one of the two components of a mixture forms a polarogram, the change of content of that compound in the course of hydrogenation can be directly determined by measurement of the height of the single wave on the polarograms of withdrawn samples; the change in content of the other component is calculated by the method explained in the example below.

Figure 2 contains a series of polarograms plotted for samples of a solution of an equimolar mixture of fumaric acid and oleic acid which had been subjected to hydrogenation; samples were taken throughout the course of the reaction at intervals corresponding to absorption of each 20-30 ml hydrogen. Only one wave changes on the polarogram — that of fumaric acid; oleic acid does not give a polarographic wave. The initial concentration of fumaric acid (as also that of oleic acid) was $250 \cdot 10^{-5}$ mole/ l. The heights of the waves of all nine curves in Figure 2 and the corresponding concentrations of fumaric acid are set forth in Table 2.

TABLE 1

No. of samples on curves	Height of wave (mm)		Maleic acid $C \cdot 10^{-5}$	Fumaric acid $C \cdot 10^{-5}$
	Maleic acid	Fumaric acid		
1	405	660	250	250
2	270	660	167	250
3	190	620	117	235
4	120	600	74	227
5	0	545	0	207
6	0	352.5	0	134
7	0	140	0	53
8	0	70	0	26

In the experimental conditions of the experiment which we describe as an example, the saturation of the weighed amounts of fumaric and oleic acids (each 0.005 g/ mole) should have required 246.2 ml hydrogen (at an air temperature of 14° and a barometric pressure of 727 mm). Such an absorption should correspond to a fall in the concentration of each of the acids, in the solutions diluted for polarogramming, from $250 \cdot 10^{-5}$ mole/l to nil. Assuming, for convenience, $1 \cdot 10^{-5}$ mole/l as unit of concentration, we may say that the concentration of each acid in these arbitrary units before the start of hydrogenation was 250 (total 500) and that after completion of hydrogenation it was 0. Hence the fall in concentration for each arbitrary unit corresponds to a hydrogen absorption of $\frac{246.2}{500} = 0.4924$ ml.

The amount of hydrogen absorbed up to the instant of withdrawal of each of the samples is known from the readings of the gas burets; we must, however, introduce a correction into these readings; on withdrawing a sample of solution for analysis, we change each time the absolute weight of unsaturated compounds participating in the reaction. In the experiment we are now considering, the first sample was taken before the start of hydrogenation; samples 2 to 8 were each taken after absorption of 20.0 ml hydrogen; sample 9 was taken after absorption of 29.2 ml hydrogen. The volume of each sample was 2 ml while that of the original solution was 40 ml. The volumes of hydrogen which would have been absorbed by the original amount of material at the instant of withdrawal of the samples are shown in Table 3, from which we see how the volumes were calculated.

TABLE 2

No. of sample and curve	Height of fumaric acid wave	Fumaric acid $C \cdot 10^{-5}$
1	370	250
2	350	236
3	310	209
4	280	189
5	240	162
6	170	115
7	110	74
8	67	45
9	0	0

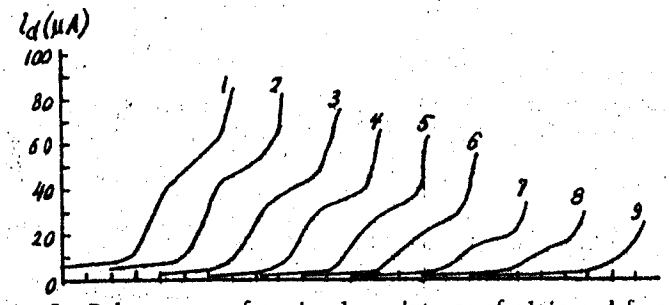

Fig. 2. Polarograms of equimolar mixtures of oleic and fumaric acids. η = 1/10. Explanation in text and Table 2.

Knowing the fall in concentration of fumaric acid at the instant of withdrawal of each sample, we calculate how much hydrogen was consumed in saturating this acid by multiplying the fall in concentration ΔC by 0.4924; the difference between the total absorption and the absorption by fumaric acid corresponds to the absorption of hydrogen by oleic acid; on dividing this difference by 0.4924, we obtain the fall in oleic concentration at the instant of withdrawal of a sample

This calculation is illustrated for a specific example in Table 4.

Consequently, in this case also, when only one of the two unsaturated components forms a polarogram, we still have the possibility of sufficiently accurately tracing the change of concentration of both components in the course of hydrogenation.

TABLE 3

No. of sample	Hydrogen absorbed (in ml)	Vol. of solution (in ml)	Formula for calculation	Total absorption of H_2 (in ml)
1	0	40	—	0
2	20	38	$\frac{20 \cdot 40}{38}$	21.1
3	20	36	$21.1 + \frac{20 \cdot 40}{36}$	43.3
4	20	34	$43.3 + \frac{20 \cdot 40}{34}$	66.8
5	20	32	$66.8 + \frac{20 \cdot 40}{32}$	91.8
6	20	30	$91.8 + \frac{20 \cdot 40}{30}$	118.5
7	20	28	$118.5 + \frac{20 \cdot 40}{28}$	147.1
8	20	26	$147.1 + \frac{20 \cdot 40}{26}$	177.9
9	29.2	24	$177.9 + \frac{29.2 \cdot 40}{24}$	226.5

On the basis of the foregoing observations, we arrive at the conclusion that polarography enables us to follow the course of joint hydrogenation of two unsaturated compounds either when the respective saturated compounds do not give polarographic waves (as is mostly the case), or when both unsaturated compounds give sharply separated waves, or only one of the two compounds gives a polarographic wave. Experiment showed that by varying the conditions of polarography (the nature of the solvent and the pH) it is nearly always possible to an adequate extent to separate the waves of the two unsaturated compounds or to suppress one of the waves.

TABLE 4

No. of sample	Fumaric acid		Total H_2 absorption (ml)	Distribution of H_2 over		Oleic acid	
	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$		Fumaric acid	Oleic acid	$\Delta C \cdot 10^{-5}$	$C \cdot 10^{-5}$
1	250	0	0	0	0	0	250
2	236	14	21.1	6.9	14.2	29	221
3	209	41	43.3	20.2	23.1	47	203
4	189	61	66.8	30.0	36.8	75	175
5	162	88	91.8	43.3	48.5	98	152
6	115	135	118.5	66.5	52.0	106	144
7	74	176	147.1	86.7	60.4	123	127
8	45	205	177.9	100.9	77.0	156	94
9	0	250	226.5	123.1	103.4	210	40

Consequently the polarographic method of investigation is only unsuitable in cases when both unsaturated compounds do not give polarograms or when the two waves coincide or have similar reduction potentials in all the conditions of polarogramming.

Our apparatus for carrying out hydrogenations most closely resembled that of S. V. Lebedev [27] and different in minor details.

The hydrogenation vessel is a duck and differs from the normal type in the presence, apart from two openings with taps of which one serves for connecting the hydrogen buret and the other for connection to atmosphere, of a third, small lateral opening which can be tightly closed by means of a tautened rubber cap; this opening is intended for withdrawal of samples during hydrogenation. The duck was rocked 300, 225 and 150 times per minute. Hydrogenation was performed with the catalyst prepared by A. S. Ginzberg's method [28]. Through the sampling opening was introduced a weighed amount of aluminum or nickel powder; the particles of metal were washed off with 5 ml solvent (usually alcohol). Through the same opening with a pipet was introduced, depending on the circumstances, 5 or 10 ml aqueous or alcoholic solution of $PtCl_4$ or Na_2PdCl_4 of predetermined concentration. The opening was then closed with the rubber cap, the duck secured in the frame of the shaker, immersed in a thermostat and connected by a rubber tube with the hydrogen line. The experimental temperature was 25 or 40°. Through the duck was passed 500 ml hydrogen, the tap was closed, and the duck connected to atmosphere; with the help of a medicinal syringe – by means of which the rubber cap is punctured – a solution of 1/200 to 1/100 g/mole of the substances or mixture of substance to be hydrogenated is introduced; with the same syringe is also introduced a small amount of solvent in order to bring the total volume of liquid to 40 ml. After the hydrogen in the buret has been levelled to atmospheric pressure, the shaker is started and reading is started of the amount of absorbed hydrogen every 60 seconds, with the help of a timing device.

Samples are withdrawn in the following way: The shaker is stopped, the cap is punctured with the needle of a syringe, 2 ml is aspirated from the duck, and the shaker is again started. The sample is transferred to a vessel from which exactly 1 ml is withdrawn with a pipet, transferred to a moistened filter for separation of the catalyst, and repeatedly washed with the solution serving as the medium for the subsequent polarographic analysis; the volume of the filtrate is made up with the same solution to 25 ml or, more often, to 50 ml.

The first sample is withdrawn before the start of hydrogenation, the subsequent samples are taken off after each 20 ml of absorbed hydrogen.

The polarographic analysis was performed with the A-3 polarograph and with the M-7 visual polarograph. The comparison electrode was a saturated calomel electrode.

SUMMARY

1. For the purpose of investigating the selectivity characteristics in the course of hydrogenation of mixtures of unsaturated compounds, the method of polarographic analysis of samples withdrawn during the hydrogenation is proposed.

2. It is shown that the polarographic method is suitable when both components of the mixture give clearly resolved waves and also when one of the two unsaturated compounds gives a polarographic wave and the other does not give a wave.

LITERATURE CITED

[1] G. Vavon and J. Detrie, Comptes rend., 172, 1231 (1921); G. Vavon and A. L. Berton, Bull. Soc. chim., (4), 37, 296 (1925).

[2] K. A. Taipale, J. Russ. Chem. Soc., 54, 638 (1922); 56, 81 (1924); 57, 487 (1925).

[3] R. Adams, J. W. Kern and R. L. Shriner, J. Am. Chem. Soc., 47, 1147 (1925); R. Adams, and J. R. Marshall, J. Am. Chem. Soc., 50, 1970 (1928); R. Adams and T. S. Hamilton, J. Am. Chem Soc., 50, 2260 (1928).

[4] H. Adkins and W. H. Zartman, J. Am. Chem. Soc., 54, 1668 (1932).

[5] L. A. Altman and M. Nemtsov, Acta Phys. Chim., 1, 429 (1934); M. S. Nemtsov, Prog. Chem., 7, 1617 (1938).

[6] V. I. Egorova, J. Gen. Chem., 6, 1404 (1936).

[7] A. V. Lozovoi, M. K. Dyakova and T. G. Stepantsova, J. Gen. Chem., 7, 1119 (1937); A. V. Lozovoi and M. K. Dyakova, J. Gen. Chem., 8, 105 (1938); A.V. Lozovoi, M. K. Dyakova and T. G. Stepantsova, J. Gen. Chem., 9, 540 (1939); A. V. Lozovoi, J. Gen. Chem., 10, 1855 (1940).

[8] S. P. Lagerev and S. F. Babak, J Gen. Chem., 7, 1661 (1937); S. P. Lagerev and M. M. Abramov, J. Gen. Chem., 8, 1682 (1938).

[9] M. I. Ushakov and A. I. Bronevsky, J Gen. Chem., 7, 750 (1937); M. I. Ushakov and E. V. Yakovleva, J. Gen. Chem., 7, 753 (1937); M. I. Ushakov and M. Sh. Promyslov, J. Gen. Chem., 17, 1115 (1947).

[10] P. G. Ugryumov, J. Gen. Chem., 10, 1985, 1995 (1940).

[11] G. Vavon and A. Husson, Comptes rend., 176, 989 (1923); G. Vavon and S. Kleiner, Comptes rend., 177, 401 (1923); G. Vavon and D. Ivanoff, Comptes rend., 177, 453 (1923).

[12] M. I. Ushakov and E. V. Yakovleva, J. Gen. Chem., 7, 753 (1937); M. I. Ushakov, M. I. Ivanova and N. F. Kosheleva, J Gen. Chem., 8, 1870 (1938).

[13] S. V. Lebedev, G. G. Koblyansky and A. O. Yakubchik, J. Russ. Chem. Soc., 56, 265 (1924); S. V. Lebedev and A. O. Yakubchik, J. Russ. Chem. Soc., 59, 981 (1927); 60, 793 (1928).

[14] G. Dupont, Comptes rend., 156, 1623 (1913); Ann. Chim. and Phys., (8), 30 485 (1913).

[15] E. F. Armstrong and T. P. Hildith, Proc. Roy. Soc., A., 96, 137 (1919).

[16] Yu. S. Zalkind, J. Russ. Chem. Soc., 45, 1876 (1913); Yu. S. Zalkind and P. V. Pishchikov, J. Russ. Chem. Soc., 46, 1527 (1914).

[17] G. Vavon and M. Jakes, Bul. Soc. chim., (4), 37, 1124 (1925); Comptes rend., 183, 299 (1926); Bull. Soc. chim. 41, 81 (1927); G. Vavon, Bull. Soc. chim., (4), 41, 1598 (1927).

[18] M. Bourguel, Bul. Soc. chim., (4), 41, 1443 (1927).

[19] Yu. S. Zalkind et. al., J. Russ. Chem. Soc., 45, 1896 (1913); 47, 680, 688 (1915); 47, 2045 (1915); 48, 538 (1916); 49, 130 (1917); 50, 19, 23, 34 (1918); 52, 186, 191, 199 (1920); 53, 279 (1921); 62, 1643 (1930); J. Gen. Chem., 3, 573 (1933); 5, 1723, 1768 (1935); 6, 1085 (1936); 7, 470, 815, 1235 (1937); 8, 1382 (1938); 9, 855 (1939); 10, 521 (1940); 11, 92, 803 (1941); 15, 90 (1945); 17, 1858 (1947); 18, 1554 (1948).

[20] B. A. Kazansky and G. T. Tatevosyan, J. Gen. Chem., 8, 1428 (1938); 9, 1458, 2248, 2256 (1939).

[21] J. E. Muskat and B. Knapp, Ber., 64, 779 (1931).

[22] G. Vavon, Comptes rend., 152, 1675 (1911); 153, 68 (1911); Bull. Soc. chim., (4), 15, 282, 287 (1914); Comptes rend., 158, 409 (1914).

[23] H. P. Kaufmann and E. Hansen-Schmidt, Ber., 60, 50 (1927).

[24] A. A. Zinovyev, Trans. V. I. I. M. P., 1936, No. 5, 43; 1937, No. 6, 120; No. 7, 69.

[25] V. V. Ipatyev and I. F. Bogdanov, J. Gen. Chem., 6, 1651 (1936).

[26] I. F. Bogdanov and E. I. Bashkirova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1936, No. 1, 91, 109.

[27] S. V. Lebedev, J. Russ. Chem. Soc., 56, 265 (1924); M. S. Platonov, "S. V. Lebedev. Life and Work", pp. XXXVI-XLVI.

[28] A. S. Ginzberg and A. P. Ivanov, J. Russ. Chem. Soc., 62, 1991 (1930).

Received March 17, 1953

Central Asian Polytechnic Institute