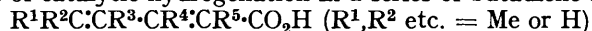


175. *Catalytic Hydrogenation of Unsaturated Compounds. Part I. Additive Mode in Relation to Selectivity of Attack and Catalyst Activity.*

By ERNEST HAROLD FARMER and ROBERT A. E. GALLEY.

THE authors have recently shown (J., 1932, 430) that at room temperature and atmospheric pressure the course of catalytic hydrogenation in a series of butadiene acids



varies from example to example; indeed the influence of the alkyl substituents in the conjugated chain on the course of the reaction appears to be as well marked in this variety of catalysed addition as in those additive processes which occur independently of, or without the intentional introduction of, catalysts. Evidence relating to plurality of additive modes in the catalytic hydrogenation of certain conjugated hydrocarbons had somewhat

earlier been advanced by Lebedev and Yakubchik (J., 1928, 832, 2192), but the nature of this evidence, striking though it was, could not be regarded as affording strict chemical proof of the dependence of additive mode on the constitution of the conjugated chain.

Quite apart, however, from any consideration of the adequacy of the experimental methods employed to demonstrate the course of reaction in the specific examples hitherto examined, there enters the important question as to how far any observed variations of additive mode in catalytic hydrogenation are dependent on the character of the conjugated chain and of the substituent groups therein (constitutive influence) and how far on phenomena related to the adsorptive power and activating capacity of the catalyst (specific catalytic influence). It is clear that no single set of measurements could decide between, or serve to allocate responsibility to, one or other of these causes in the present state of knowledge concerning (1) the influence of experimental conditions (especially temperature and pressure) on the functioning of the catalyst, and (2) the extent to which changes in the physical condition or in the substance (including poisoning) of the catalyst can engender corresponding variation in additive reactivity. The authors are primarily concerned with elucidating the nature and characteristics of the constitutive influence and it has been convenient as a first step in this direction to gain some idea of the importance to be attached to the two types of influence as active orienting factors by observing the course of reaction under arbitrarily selected conditions of operation; and because of the ease with which large numbers of comparative hydrogenations can be carried out at atmospheric pressure and room temperature (approx.) without serious difficulty in maintaining a reasonably uniform degree of activity of the catalyst, these conditions of reaction have been adopted.

A dual or multifold mode of hydrogen addition such as applies to the members of the sorbic acid series of conjugated compounds amounts of course to *selectivity* in hydrogenation—a phenomenon which has already been the subject of observation amongst varied types of multi-unsaturated compounds (cf. Vavon and his collaborators, *Compt. rend.*, 1910, 150, 1127; 1911, 152, 1675; 1911, 153, 68; Armstrong and Hilditch, *Proc. Roy. Soc.*, 1925, A, 108, 121; Paal, *Ber.*, 1912, 45, 2221). In order, however, to trace the constitutive influence on the course of hydrogen addition to conjugated compounds it is necessary as a practical measure, not only to examine the comparative behaviour of the latter themselves in the manner described in the authors' previous paper (*loc. cit.*), but also to place beyond doubt the order of reducibility (if any such exists independently of specific catalytic influence) of conjugated compounds compared with ethylenic compounds and also of ethylenic compounds (*e.g.*, Δ^{α} -, Δ^{β} -, and Δ^{γ} -acids) compared with one another. Further it is necessary to examine the effect on the course of reaction of submitting the catalyst to treatment in ways which might be supposed to affect its activity (cf. the experiments of Vavon on the influence of catalyst poisons, *Bull. Soc. chim.*, 1914, 15, 282; *Compt. rend.*, 1922, 175, 277. See also Armstrong and Hilditch, *Trans. Faraday Soc.*, 1922, 17, 670; Taylor, *Proc. Roy. Soc.*, 1925, A, 108, 105). Throughout the work here described the quantitative determination of the components of reduction mixtures has been effected so far as practicable by degradative analysis, a procedure capable of considerable accuracy for unsaturated carboxylic acids and one essential to the confirmation of conclusions based on variations in the rate of hydrogen absorption.

Selective Hydrogenation in Mixtures of Mono-olefinic Substances.—As the result of hydrogenations carried out with a platinum catalyst under standard conditions of operation, Lebedev, Kobliansky, and Yakubchik (J., 1925, 127, 417) have concluded that the main factor which determines the rate of reduction of individual olefins is the degree of substitution: thus mono-, di-, tri-, and tetra-substituted olefinic compounds are reduced at rates which diminish for the respective compounds in the order given; also in mixtures of olefins, monosubstituted compounds are reduced preferentially to di-, di- to tri-, and tri- to tetra-substituted compounds. The *principle of consecutive reduction* embodied in the last portion of this statement rests solely, at present, on the approximate correspondence of points of break in the curves showing rate of hydrogen absorption throughout the reduction process (rate-time curves) with the points of break which are theoretically to be expected on the assumption that the components of the mixture are hydrogenated consecutively at different rates (see, for example, curve III, Fig. 4). In a number of cases, however, which the

authors have examined, the observed points of break agree so imperfectly (and the imperfections are not found to disappear in any repetitions of the experiments) with the points calculated from the composition of the mixtures that further evidence of the reliability of the principle appeared necessary before accepting its presumed bearing on the complex mode of reduction (generally three-fold) of butadienoid compounds. Such additional evidence is afforded by the examination of (a) the Δ^{α} -, Δ^{β} -, and Δ^{γ} -forms of hexenoic acid (I, II, and III respectively), all of which are theoretically obtainable dihydrogenation products of sorbic acid (IV), (b) Δ^{γ} -pentenoic acid (V), a dihydrogenation product of β -vinyl-acrylic acid (VI), and (c) allyl alcohol. It is to be noted that the three hexenoic acids are symmetrically disubstituted olefins, and Δ^{γ} -pentenoic acid and allyl alcohol are mono-substituted.



The variation in the rate of hydrogen absorption from minute to minute of the saturation process is shown for the above-named substances in Figs. 1—5. All the curves, unless

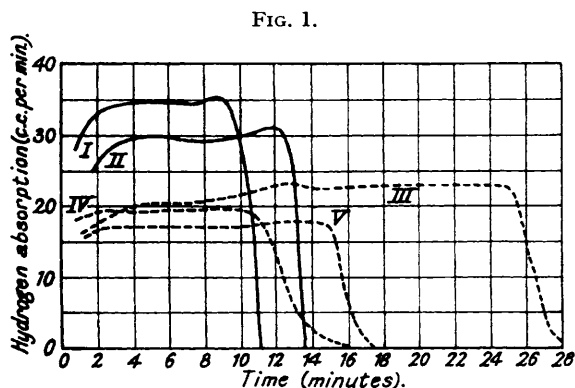


FIG. 1.—Hydrogenation of (a) Δ^{γ} -pentenoic acid (curves I and II represent successive reductions with the same catalyst specimen), and (b) Δ^{α} -hexenoic acid (curves III and IV represent successive reductions with a catalyst specimen freshly prepared from platinum oxide, and curve V a similar reduction carried out after the lapse of $\frac{1}{2}$ hour).

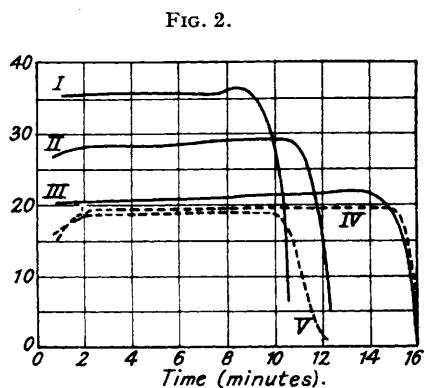


FIG. 2.—Hydrogenation of (a) Δ^{β} -hexenoic acid (curve I represents reduction in a considerably diluted medium; curve II reduction carried out immediately after the latter with the same catalyst specimen, but under standard conditions; curve III reduction with a catalyst which had just previously been used to reduce Δ^{γ} -hexenoic acid), and (b) Δ^{γ} -hexenoic acid (curve IV represents reduction with a catalyst which had just previously been used to reduce Δ^{γ} -pentenoic acid; curve V, reduction with the same catalyst specimen immediately afterwards).

otherwise denoted, refer to standard conditions of operation, detailed on p. 694, and it is important to state that (within the limits of the authors' observations) the concentration of the unsaturated substance in the alcoholic medium employed has no measurable effect on the rate of hydrogenation—as indeed would be anticipated from the fact that the rate of hydrogen absorption is remarkably constant *throughout* the reduction of most mono-olefinic substances. The following points, of which the first two are well known in connexion with other catalysed reactions, are to be noted: (1) The maximum speed of hydrogen absorption is not attained in the early stages of the employment of a catalyst which has been newly reduced from the oxide (see curve III, Fig. 1), so that some previous use of the catalyst, or at any rate the lapse of a period during which the catalyst is allowed to remain in contact with hydrogen in the reducing medium, is desirable before the catalyst is employed in the study of preferential hydrogenation. (2) The catalyst may be conveniently used several times successively in short reductions (either of the same substance or of

substances of related types),* since the activity of the catalyst as measured by the rate of hydrogen absorption diminishes rather slowly with use; but after prolonged use the activity seriously deteriorates. (3) With the three hexenoic acids, all of which are disubstituted olefins, the rate of hydrogen absorption increases with increasing remoteness of the double bond from the carboxyl group: this is illustrated in Fig. 5, the curves in which were obtained in consecutive reductions with the same specimen of catalyst, starting with the least rapidly reduced acid; here, of course, owing to slow progressive loss of activity by the catalyst the maximum differences in rate of reduction may not have been attained. The curves for allyl alcohol (curves I and II, Fig. 4), and to a less extent those for Δ^{β} -hexenoic acid (curve I, Fig. 2) and Δ^{γ} -pentenoic acid (curves I and II, Fig. 1), show a sudden increase in the rate of hydrogen absorption just before saturation is complete and consequently when the concentration of unsaturated material is quite small. This feature, the cause of which is not apparent, is especially characteristic of the named substances when the catalyst is highly active and had already been noted in the case of allyl alcohol by Lebedev, Kobliansky, and Yakubchik (*loc. cit.*). (5) Δ^{γ} -Pentenoic acid is hydrogenated at a more rapid rate under standard conditions than the three hexenoic acids.

FIG. 3.

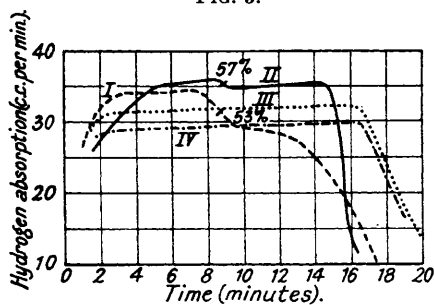


FIG. 3.—Hydrogenation of equimolecular mixtures of (a) Δ^{γ} -pentenoic and Δ^{α} -hexenoic acids (curve I), (b) Δ^{γ} -pentenoic and Δ^{β} -hexenoic acids (curve II), and (c) Δ^{α} - and Δ^{γ} -hexenoic acids (curve III). Hydrogenation of "dihydrosorbic acid" is represented in curve IV.

FIG. 4.—Hydrogenation of (a) allyl alcohol (curves I and II represent successive reductions with the same catalyst specimen), and (b) an equimolecular mixture of allyl alcohol and Δ^{α} -hexenoic acid (curve III).

FIG. 4.

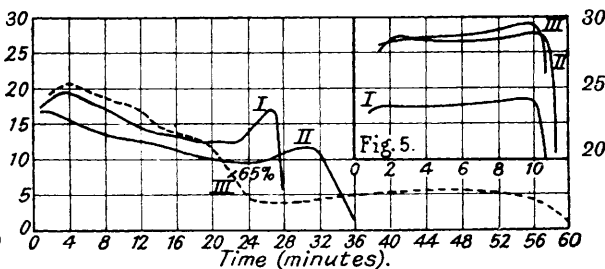


FIG. 5.

Fig. 5.—Relative rates of reduction of Δ^{α} -, Δ^{β} -, and Δ^{γ} -hexenoic acids (curves I, II, and III respectively). Reductions carried out in rapid succession with the same catalyst specimen.

Turning to the question of preferential reducibility in mixtures of mono-olefinic substances, the experimental results are striking. The hydrogenation curve (rate-time) for an equimolecular mixture of Δ^{α} - and Δ^{γ} -hexenoic acids is a smooth one, showing no break at the point representing 50% saturation; similarly the curve for ordinary hydrosorbic acid (produced by the reduction of sorbic acid with aluminium amalgam), which consists approximately of 60% of Δ^{β} - and 40% of Δ^{γ} -hexenoic acid, is also quite smooth. On the other hand the hydrogenation curve for an equimolecular mixture of Δ^{γ} -pentenoic acid and Δ^{α} -hexenoic acid (curve I, Fig. 3) shows a break at about 53% hydrogenation, and that of an equimolecular mixture of Δ^{γ} -pentenoic and Δ^{β} -hexenoic acids (curve II, Fig. 3) shows a break at about 57% hydrogenation. These results suggest that the components of the first two mixtures, which are of the same degree of substitution, are hydrogenated side by side, at the same, or nearly the same, rate, whereas those in the second two, which are of different degrees of substitution, are hydrogenated (for the most part at any rate) consecutively. The evidence here afforded is precisely similar to that which was accepted by Lebedev, Kobliansky, and Yakubchik (*loc. cit.*) as the basis of the principle of consecutive reduction already mentioned.

The course of reaction in these examples was placed beyond doubt by oxidising the

* The rate of hydrogenation, however, of a substance B appears in certain cases to be capable of very serious diminution if the product of hydrogenation of a previously reduced substance A is allowed to remain in the reducing medium (see below).

various partial hydrogenation products with permanganate. In each case the character and proportions of the fission products arising from the unreduced olefinic material showed with considerable accuracy the percentage of each of the original components which had undergone hydrogenation. It was quite clear that the components of each of the binary mixtures of isomeric hexenoic acids had been hydrogenated concurrently at equal or nearly equal rates; it was equally definite that the less highly substituted olefinic component of the binary mixtures containing pentenoic acid with one or other of the isomeric hexenoic acids had suffered preferential hydrogenation to a degree of completeness equalling *at least* 98% of the whole. Thus the position of the double bond with respect to the carboxyl group appears to have little influence on the preferential reducibility of the acid so long as the degree of substitution at the double bond remains unchanged.

An example which has an important bearing on the problem of selectivity is afforded by the reduction of an equimolecular mixture of allyl alcohol and Δ^{α} -hexenoic acid. Allyl alcohol, although a monosubstituted olefin, undergoes hydrogenation relatively slowly; Δ^{α} -hexenoic acid, on the other hand, undergoes hydrogenation relatively rapidly. If, therefore, the intrinsic speeds of reduction of the separate components were the all-important factor in determining selectivity, the principle of consecutive reducibility would break down in this example. Actually, however, the principle does not break down. The mixture was found to absorb hydrogen readily at first (see curve III, Fig. 4), but absorption then fell off fairly rapidly and a distinct break in the rate-time curve occurred at approximately 65% hydrogenation; after that, absorption was very slow, corresponding, as was thought at first, with the hydrogenation of allyl alcohol. Chemical degradation of the products obtained by hydrogenating the mixture up to the point of break in the curve (point X) showed, however, quite conclusively that the material remaining unreduced at this point was not allyl alcohol but pure Δ^{α} -hexenoic acid: therefore, hydrogenation had occurred selectively at the double bond of allyl alcohol in spite of its low normal rate of hydrogenation. Why the rate of hydrogenation of the hexenoic acid thus left behind should fall to the low value observed is not clear, but the example points very definitely to the relative unimportance of the absolute speed of hydrogenation in determining selectivity.

Selectivity amongst Competing Mono-olefinic Conjugated Systems.—The authors' earlier examination of the partial hydrogenation products of sorbic acid and those of its homologues (*loc. cit.*) had indicated that the formation of the fully saturated derivative of each conjugated acid *begins* at the *outset* of reaction; for this reason $\alpha\beta\gamma\delta$ -additivity (*i.e.*, simultaneous addition at both ethylenic centres) was attributed as one of the characteristic reactivities of the series. Owing to the occurrence of this type of additivity the absorption of one molecule of hydrogen by sorbic acid left 44% of the conjugated acid unchanged—a proportion which remained remarkably constant under the usual conditions of operation. Accepting this figure, and assuming a rate of disappearance of sorbic acid strictly proportional to the amount of hydrogen absorbed, it would be expected that all the sorbic acid would disappear at the stage of 93% hydrogenation, *i.e.*, only shortly before complete saturation. This expectation was entirely fulfilled in practice and it was found, moreover, that at eight other points between 0% and 93% hydrogenation the quantity of residual sorbic acid actually isolated corresponded extremely closely with that calculated on the same basis. The linear curve connecting disappearance of sorbic acid with hydrogen absorption is shown in Fig. 6.

Simultaneously with the disappearance of sorbic acid a mixture of saturated and unsaturated acids is always produced, and it has been possible by first separating the residual sorbic acid from a number of partly hydrogenated products and then estimating the relative amounts of monoethylenic and saturated material contained therein, to show (see Fig. 6) that the formation of ethylenic and of saturated material occurs at uniform but different rates up to the point at which the conjugated material entirely disappears; after this point the ethylenic material suffers hydrogenation. Owing to the relatively small proportion of total ethylenic material produced, and to difficulties attending the exact estimation of its component acids, it has not been possible to draw separate curves showing the relative incidence of $\alpha\beta$ -, $\alpha\delta$ -, and $\gamma\delta$ -addition as hydrogenation proceeds.

The question then arises: does *any* reduction of ethylenic material occur before all the

conjugated material has disappeared, or, in other words, does the formation of a proportion of the saturated material occur *from the outset of reaction* in two stages, *viz.*, first by dihydrogenation to produce the three isomeric hexenoic acids, and then by further reduction of one or all of these to produce hexoic acid? On the answer to this question depends the degree of selectivity which can be assumed to exist between the conjugated and the ethylenic acid.

There is nothing about the relationship of the individual curves in Fig. 6 to preclude the possibility that to some small but constant extent hydrogenation of the derived mono-olefinic material occurs simultaneously with the tetrahydrogenation process from the outset of reaction. Were this the case, however, the point at which the conjugated acid disappeared (93% hydrogenation) must necessarily change, if, instead of sorbic acid, a mixture of sorbic acid with one or other of the three isomeric hexenoic acids were initially taken. A series of reductions carried out with mixtures of sorbic acid and Δ^{α} -hexenoic acid, and of sorbic acid and Δ^{β} -hexenoic acid, showed quite clearly that the point of disappearance of the sorbic acid is not appreciably changed from that previously observed (93% hydrogenation); furthermore the proportions of sorbic acid remaining at different stages during the

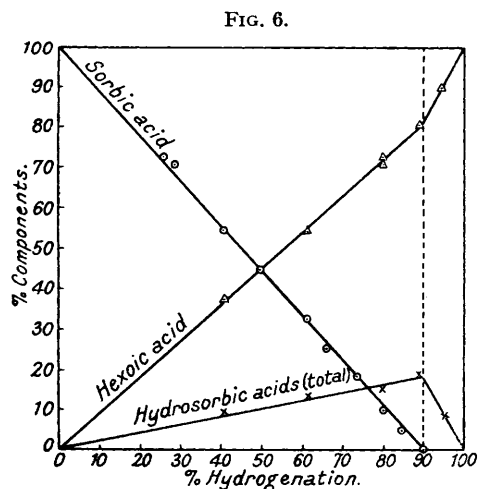
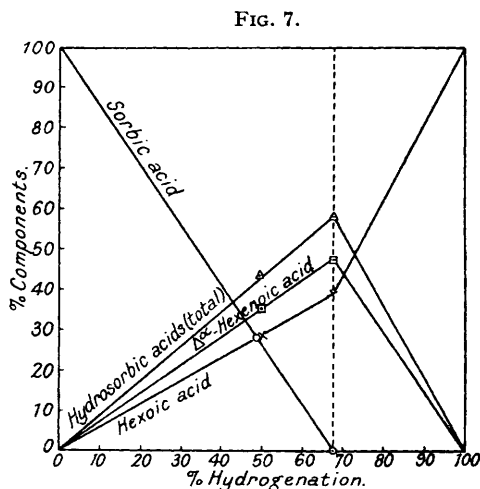


FIG. 6.—Change of composition of reduction mixture during hydrogenation of sorbic acid (new catalyst).
 FIG. 7.—Change of composition of reduction mixture during hydrogenation of sorbic acid ("aged" catalyst).



reduction were found to agree exactly with those which would have obtained if no ethylenic acid had been initially taken. Thus, within the limits of accuracy imposed by the separative and degradative procedures employed (*i.e.*, in so far as concerns at least 98% of the conjugated material taken), it is correct to state that *all* of the fully saturated material which is produced before the conjugated material has become entirely used up, is formed by the simultaneous reduction of both ethylenic bonds of the conjugated acids. Accordingly there is no doubt as to the preferential or selective reduction of sorbic acid before that of its dihydrogen derivatives and presumably also of other mono-olefinic substances; moreover the present indications are that a similar statement could also be made for the homologues of sorbic acid, but this has not yet been systematically verified.

Specific Activity of the Catalyst.—It has been stated that the platinum catalyst deteriorates slowly with use in respect of the rate at which hydrogenation is effected, but usually a sample of catalyst can be employed several times in the reduction of a few grams of one or other of the acids under examination without the deterioration becoming serious; with prolonged use, however, the rate at which hydrogenation can be effected markedly decreases. The lowering in activity may be due to active patches in the catalyst becoming either inactive or much less active (cf. Rideal, J., 1922, 121, 309; Pease, *J. Amer. Chem. Soc.*, 1923, 45, 1196, 2235; Armstrong and Hilditch, *Trans. Faraday Soc.*, 1922, 17, 670; Taylor,

Proc. Roy. Soc., 1925, A, **108**, 105) and it is possible that definite stages of deactivation analogous to those achieved by Vavon and Huson (*Compt. rend.*, 1922, **175**, 277) by carbon disulphide poisoning are capable of being progressively realised. Thus two substances might conceivably be found, of which one could be hydrogenated in the presence of a freshly reduced catalyst, but not in the presence of a more "aged" sample,* whilst the other could be hydrogenated in the presence of either catalyst but less rapidly in the presence of the more aged. It remains therefore to be seen whether different states of activity in the catalyst, as denoted by difference in the speed of promoting reduction of unsaturated substances, can have a specific effect on the additive mode of a conjugated compound, or whether the additive mode is entirely dependent on the conjugated constitution.

Experiment with sorbic acid and a catalyst which had been applied many times to the reduction of ethylenic acids and then allowed to stand for many weeks in contact with a reduction mixture (*i.e.*, not merely a "slightly aged" specimen), showed at once that already at the stage of 68% hydrogenation only a negligible quantity of unchanged acid remained, instead of about 27% as was expected on the basis of the previous experiments; repetition of the experiment gave the same result, although when freshly reduced catalysts were substituted for the aged specimens, the previously described results were again obtained. A new quantity of catalyst was therefore aged in, as nearly as possible, the same way as before: samples of this catalyst, which behaved similarly to the aged samples mentioned above, were used for determining in detail the additive behaviour of sorbic acid. This behaviour differed very considerably from that observed when a newly reduced catalyst was in use: the percentage composition of the reduction product at the stage 50% hydrogenation is shown for aged and new catalysts in the table, and a diagrammatic

Composition of hydrogenation product of sorbic acid (%) (50% hydrogenation).

| Acid. | Additive type. | New catalyst. | Old catalyst. |
|-----------------------------------|---------------------------|---------------|---------------|
| Sorbic | — | 44 | 28 |
| Hexoic | $\alpha\beta\gamma\delta$ | 44 | 28 |
| Δ^{α} -Hexenoic | $\gamma\delta$ | 7 | 36 |
| Δ^{β} -Hexenoic | $\alpha\delta$ } | 5 | 8 |
| Δ^{γ} -Hexenoic | $\alpha\beta$ } | | |

representation of the whole course of reduction in the presence of the aged catalyst in Fig. 7. By comparison of this diagram with that in Fig. 6 it is clear that the degree of simultaneous reduction of the two ethylenic bonds is greatly diminished when the catalyst is aged, and correspondingly the proportion of ethylenic material is increased. From the table it is seen that the increase in the proportion of ethylenic material is caused mainly by increase in the amount of $\gamma\delta$ -addition, the amounts of $\alpha\beta$ - and $\alpha\delta$ -addition being little changed.

It appears, therefore, that the selective action of a catalyst in promoting the reduction of a monosubstituted olefin before that of a more heavily substituted one, or the reduction of a conjugated polyolefin before that of a mono-olefin, is a permanent characteristic which is quite distinct from the specific activating capacity of the particular catalyst specimen employed, which affects the additive mode of a polyolefin. Thus, whereas the "activity" of the catalyst affects only the rate of hydrogenation of a mono-olefin, it can affect both the rate of hydrogenation and the additive mode of a conjugated compound.

In explanation of the foregoing results it is now suggested that the activation produced at each of the ethylenic centres of a conjugated substance by a highly active catalyst may be sufficiently potent to initiate addition simultaneously at both centres (the degree of activation at each is not necessarily the same) quite independently of any augmenting activation, and in spite of any deactivating influence, arising from the substituents present in the carbon chain. Possibly the failure of Paal (*Ber.*, 1912, **45**, 2221) to effect the *step-wise* reduction of conjugated compounds with a platinum catalyst is to be attributed to the high state of activity of the latter, which promoted *complete* saturation in one stage. With catalysts of a lower degree of activity (*e.g.*, the catalysts used in this investigation, and more particularly the "well-aged" catalyst), however, the constitutive or substitutional influence appears to be capable of assuming a greatly enhanced relative importance and might be

* Aged by lapse of time since preparation or by previous use.

expected to attain its maximum value in the case of a catalyst which can only just promote reduction. Presumably the activating or deactivating impulses thus directed by the substituents towards one or other of the ethylenic centres of the chain are superimposed on the activations due to the catalyst, so effectively modifying the additive mode.

Probably therefore no characteristic mode of hydrogen addition can be ascribed to sorbic acid and its homologues independently of the degree of activity of the catalyst, although an approach towards diagnosing the purely constitutional influences on the course of reaction may conceivably be possible by effecting hydrogenation with catalysts of a low degree of activity. But although the figures expressing variable additive tendencies given in the authors' previous paper do not necessarily reflect solely the differences in constitution between the different conjugated acids—a fact made clear in the present investigation by the change in the ratio of $\gamma\delta$ -addition to $\alpha\beta$ - + $\alpha\delta$ -addition for sorbic acid from 1.4 : 1 to 4.5 : 1—it is nevertheless certain that the differences in constitution correspond to differences in orienting influence which are potentially, at least, of very considerable importance.

EXPERIMENTAL.

Standard Conditions of Hydrogenation.—The reaction vessel was a 200 c.c. Pyrex flask mounted in a shaker capable of maintaining a reasonably uniform rate of oscillation at speeds between 120 and 150 oscillations per min. The medium consisted of rectified spirit (75 c.c., except where otherwise stated) and the platinum catalyst was prepared in 0.1 g. portions as required by shaking an alc. suspension of hydrated platinum oxide, $\text{PtO}_2 \cdot \text{H}_2\text{O}$ (Adams, "Organic Syntheses," VIII, 92), with well-washed H in the reaction vessel. Since the rate of hydrogenation of a substance is not an absolute characteristic, but varies with the rate of shaking, the amount of catalyst, and the vol. of solution in relation to the size and shape of the reaction vessel, it was necessary in all comparisons of reduction velocity to adhere rigidly to the standard conditions. For comparative expts. in which a uniform degree of activity of the catalyst was so far as possible to be maintained, the catalyst specimens employed were taken from the same batch of oxide. The hydrogenation of the various unsaturated compounds, and especially of the conjugated compounds, was accompanied by evolution of heat; the temp. generally rose about 10° , but with increased "ageing" of the catalyst, the temp. increase was less marked. At the end of the hydrogenation process a portion of the catalyst was usually retained in colloidal solution; when, however, the catalyst had previously been used for hydrogenation, it settled out quickly, and could be completely separated by decanting the supernatant liquor. The alcohol was removed from the reduction products by distillation at reduced pressure.

Partial Hydrogenation with an Active ("New") Catalyst.

Separation and Oxidation of Products.—Since the methods employed in separating the various partial hydrogenation products (mixtures of saturated and unsaturated material containing from two to five components) obtained in the course of this work resembled closely those described in the authors' previous paper (*loc. cit.*), the manipulative details are for the most part omitted here. The oxidation of the unsaturated material contained in the products was invariably effected with 3% KMnO_4 aq. at 0° after the product had been freed from solvent.

Mixtures of Δ^α -Hexenoic Acid and Δ^γ -Pentenoic Acid.—*Expt. 1.* An equimol. mixture of the acids was hydrogenated with half the quantity of H required for complete saturation. The reduction product yielded on oxidation butyric, valeric and oxalic acids, all of which were readily isolated; no succinic acid, arising from unchanged Δ^γ -pentenoic acid, could be found.

Expt. 2. A similar equimol. mixture containing 1.93 g. and 1.71 g. of the respective acids was 50% hydrogenated (383 c.c. H) * under equiv. conditions. On oxidation, the three acids previously isolated were again obtained, the yield of oxalic acid (as estimated by titration of an aliquot part of the oxidation liquor with $N/10$ - KMnO_4 at 60°) corresponding to the survival in the reduction mixture of 1.8 g. of Δ^α -hexenoic acid. No trace of succinic acid could be found.

Expt. 3. A mixture containing 4.26 g. and 1.6 g. of the respective acids (*i.e.*, not equimol.) was treated with just sufficient H to saturate the minor component of the mixture, *i.e.*, the Δ^γ -pentenoic acid. By careful distillation of the reduction product, nearly the whole (4 g.) of the Δ^α -hexenoic acid was recovered unchanged (m. p. 33 – 35°).

Mixtures of Δ^β -Hexenoic Acid and Δ^γ -Pentenoic Acid.—An equimol. mixture of the acids (2.3 g. and 2.14 g. respectively) was semi-hydrogenated (480 c.c. of H). The product yielded on oxidation at 0° with dil. KMnO_4 aq., propionic acid, valeric acid, and a small quantity of

* The vol. of H supplied, both here and in subsequent expts., refers to *N.T.P.*

oxalic acid; no succinic acid could be isolated, although it was found by *ad hoc* expts. that small quantities of succinic acid (*e.g.*, 0.05 g.), when admixed with a larger quantity of oxalic acid (*e.g.*, 0.5 g.) and the whole submitted to the action of $N/10\text{-KMnO}_4$ at 60° , could still be isolated in sufficient quantity to ensure satisfactory identification. The oxalic acid formed could only have been derived from the Δ^β -hexenoic acid, and indeed it was found that pure specimens of this acid (m. p. 12.5°) always suffered fission with permanganate to yield some quantity of oxalic acid in place of malonic acid, and a good yield of propionic acid, the complementary product of malonic acid.

Mixtures of Δ^α -Hexenoic Acid and Allyl Alcohol.—*Expt. 1.* An equimol. mixture of these substances was hydrogenated until the rate of absorption had fallen from more than 20 c.c. to 5 c.c. per min. (see Fig. 4). The product, when oxidised, yielded oxalic acid, a large amount of butyric acid, and a trace of a pungent-smelling acid. Obviously, therefore, the allyl alcohol had mainly been hydrogenated.

Expt. 2. The hydrogenation of a mixture of 1.34 g. of Δ^α -hexenoic acid and 0.75 g. of allyl alcohol was stopped at the point when the change from rapid to slow absorption occurred. The product, when oxidised, yielded butyric acid, oxalic acid, and a small quantity of hexoic acid, but the quantities of these showed that at least 1 g. of the Δ^α -acid had escaped hydrogenation.

Mixtures of Δ^α - and Δ^γ -, also of Δ^β - and Δ^γ -Hexenoic Acids.—The smoothness of the hydrogenation curves for these mixtures (shown in Fig. 3, curves III and IV) indicates that the components in each case suffered attack side by side as though they did not differ in composition. When a mixture of the Δ^α - and the Δ^γ -acid (2.92 g.) was 50% hydrogenated and the product oxidised, a mixture of acetic, butyric, hexoic, oxalic, and succinic acids was obtained, in which the amount of oxalic acid (estimated by means of $N/10\text{-KMnO}_4$ at 60°) was that derivable by the oxidation of 1.36 g. of Δ^α -hexenoic acid. Thus both of the unsaturated acids suffered attack at the same, or very nearly the same, rate.

Mixtures of Sorbic Acid with Various Hexenoic Acids.—*Expt. 1.* To a mixture of 5.6 g. of sorbic acid and 3.6 g. of Δ^β -hexenoic acid, 2020 c.c. of H (90% of that required for saturating the sorbic acid alone) were added. On removal of the solvent and fractional distillation of the reduction product, only 0.1 g. of sorbic acid remained. When, for comparison, specimens of sorbic acid unadmixed with hexenoic acid were similarly treated with 90% of the hydrogen necessary for complete saturation, the proportion of sorbic acid recovered did not differ appreciably from that found above.

Expt. 2. 4100 c.c. of H were added to a mixture of 11.2 g. of sorbic acid and 3.4 g. of Δ^β -hexenoic acid: only 0.1—0.2 g. of sorbic acid escaped hydrogenation.

Expt. 3. A mixture of 5.6 g. of sorbic acid and 3.6 g. of Δ^α -hexenoic acid, when treated with half the quantity of H requisite to saturate the sorbic acid alone, yielded only 2.4 g. of unchanged sorbic acid. Oxidation of the liquid acids contained in the reduction product yielded a quantity of oxalic acid which, when estimated by titration of an aliquot portion of the oxidation liquor with $N/10\text{-KMnO}_4$ at 60° , corresponded to the presence in the reduction product of 3.65 g. of unchanged Δ^α -hexenoic acid.

Expt. 4. A mixture of 5.6 g. of sorbic acid and 3.8 g. of Δ^β -hexenoic acid was supplied with 66% of the H required for saturating the sorbic acid alone. From the reduction product, only 1.5 g. of sorbic acid was recovered, whilst by oxidation of the residual material a large quantity of propionic acid was obtained. This showed directly that the reduction product had contained a large proportion of Δ^β -hexenoic acid, although the exact amount was not in this case estimated.

Partial Hydrogenation with an "Aged" Catalyst.

Sorbic Acid.—When specimens of this acid were treated with 66% of the H required for complete saturation, no residual sorbic acid could be isolated on fractionally distilling the product.

Mixture of Sorbic Acid and Δ^α -Hexenoic Acid.—When a mixture of 5.6 g. of sorbic acid and 2.5 g. of Δ^α -hexenoic acid was treated with 66% of the amount of H necessary to saturate the sorbic acid alone, again no trace of the latter acid could be isolated on working up the product. When the expt. was repeated using the same respective quantities of acids but only 50% of the H necessary to saturate the sorbic acid alone, 1.5 g. of sorbic acid were recovered; this amount was exactly equal to that recoverable when 5.6 g. of sorbic acid alone were 50% hydrogenated. The oxidation product of the 50% hydrogenated mixture contained an amount of oxalic acid equivalent to 4.3 g. of Δ^α -hexenoic acid, which is less by 0.3 g. (owing to the formation of some hexoic acid and minor amounts of Δ^β - and Δ^γ -hexenoic acids from the sorbic acid) than the sum of the amount of Δ^α -acid originally present and that producible from the sorbic acid if only $\gamma\delta$ -dihydrogenation occurred.

The Course of Hydrogenation of Sorbic Acid.

With an Active ("New") Catalyst.—Portions of sorbic acid were submitted to the action of different amounts of H (approximately 25, 30, 40, 60, 75, 80, 90, 95% of that required for saturation). The amounts of (a) unchanged sorbic acid, (b) hexoic acid, (c) total mono-olefinic acid, and (d) Δ^{α} -hexenoic acid were determined and from the values obtained a diagram summarising the course of hydrogenation (Fig. 6) was constructed. The values in the categories (a) and (b) were determined by direct separation of the products concerned, those in (c) by determining the amount of H required to saturate the mono-olefinic residues, and those in (d) by titrating with KMnO_4 at 60° the oxalic acid produced on oxidising the mono-olefinic portions of the reduction products. The values in (d) may be slightly too large owing to the tendency of Δ^{β} -hexenoic acid (here produced in small amount) to give a little oxalic acid on oxidation.

In order to test the reproducibility of the foregoing results with sorbic acid and thus to ensure that a reasonable uniformity in the degree of activity of the catalyst could be maintained, a similar but shorter series of reductions was carried out with portions of catalyst from two entirely new preparations of hydrated platinum oxide. In all cases the values for recovered sorbic acid and those for hexoic acid and mono-olefinic material agreed very closely with the corresponding values derived from Fig. 6.

With an "Aged" Catalyst.—By carrying out a similar series of partial hydrogenations employing a catalyst "aged" by previous use, a diagram summarising the course of reduction of sorbic acid with a less active catalyst was constructed. This diagram (Fig. 7) shows a course of reduction differing materially from that observed with a "new" catalyst.

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IMPERIAL COLLEGE, LONDON, S.W. 7.

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