USE OF OLEFINS FROM PETROLEUM IN THE SYNTHESIS OF ORGANIC ACIDS AND THEIR DERIVATIVES

BY

G. NATTA, P. PINO AND R. ERCOLI

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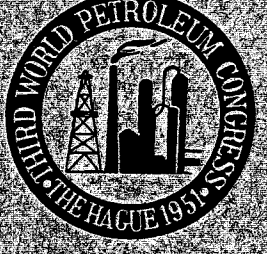
SECTION V



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USE OF OLEFINS FROM PETROLEUM IN THE SYNTHESIS OF ORGANIC ACIDS AND THEIR DERIVATIVES

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G. NATTA *, P. PINO AND R. ERCOLI

Synopsis

The study of the reaction between olefins, CO and alcohols has allowed us to determine the conditions in which the formation of esters of acids with one carbon atom more than the initial olefin is prevalent, and those in which prevails the formation of products due to parallel reactions.

When olefins higher than ethylene and primary alcohols, particularly methanol, are used, the ester formation prevails. With asymmetric olefins (e.g. propylene), mixtures of esters (e.g. n. butyrate and iso-butyrate, with prevalence of the former) are formed. With alcohols higher than methanol, which are more easily dehydrogenatable, the secondary reaction products (oxo-synthesis) increase, because kinetically the oxo-synthesis reaction is faster than the carboxylation reaction.

In case of the use of secondary alcohols, the oxo-synthesis reaction prevails upon the carboxylation reaction also in the absence of hydrogen.

When the reaction between CO, olefins and alcohol is performed in the presence of hydrogen, the oxo-synthesis reaction leads predominantly to the direct formation of alcohols with one carbon atom more than the starting olefin. The alcohol used as initial material is dehydrogenated to a less extent than corresponds to the hydrogen absorbed in the alcohol hydrogenation of the aldehyde obtained by oxo-synthesis.

When operating in the absence of hydrogen with too small a proportion of CO with respect to the olefins with n. carbon atoms, under certain conditions the synthesis of ketones with 2 n + 1 carbon atoms may prevail. For example, with ethylene, CO and methanol yields have been obtained upwards of 50% diethyl ketone, with simultaneous formation of 20% methyl propionate.

For the reaction of CO and amines the carboxylation of olefins leads to the formation of amides and kinetically this reaction is faster than carboxylation with CO and ester alcohols.

Whereas the synthesis of aldehydes from olefins by carboxylation with CO and H_2 is already extensively applied in industry, we feel that other interesting products, esters, amides, ketones, alcohols, can also be produced directly by synthesis from olefins and CO whenever the reaction is carried out in the presence of alcohols or amines.

* Istituto di Chimica Industriale Politecnico, Milan, Italy.

Résumé

L'étude de la réaction entre les oléfines, le CO et les alcools, a permis de déterminer les conditions dans lesquelles se forment surtout des esters d'acides, ayant au début un atome de carbone de plus que les oléfines, ou plutôt des produits dûs à des réactions secondaires.

En employant des oléfines supérieures à l'éthylène et des alcools primaires, surtout le méthanol, la formation d'esters prédomine; avec des oléfines asymétriques (par exemple le propylène) il se forme des mèlanges d'esters (par exemple, de l'acide butyrique normal et de l'acide isobutyrique, le premier surtout); avec des alcools supérieurs au méthanol, susceptibles d'être déshydrogénés plus facilement, les produits secondaires se forment en plus grande proportion (oxo-synthèse) parce que la réaction d'oxo-synthèse s'accomplit toujours plus vite que celle de carboxylation.

En utilisant les alcools secondaires, la réaction d'oxo-synthèse prédomine par rapport à celle de carbonylation même en absence d'hydrogène.

En faisant réagir du CO, des oléfines et de l'alcool avec de l'hydrogène, la réaction d'oxo-synthèse donne d'abord des alcools ayant un atome de carbone de plus que l'oléfine de départ.

Quand on opère dans les mêmes conditions avec seulement des oléfines, du CO et du H_2, on obtient surtout des aldéhydes.

L'alcool de départ est déshydrogéné dans une plus

faible proportion que l'hydrogène n'est absorbé dans l'hydrogénation des aldéhydes en alcools.

En opérant sans hydrogène et avec un manque de CO sur des oléfines à n atomes de carbone, la formation de cétones à 2 n + 1 atomes de carbone peut, dans certains cas, prédominer.

Ceci est illustré par le fait que, avec l'éthylène, du CO et du méthanol, on a obtenu des produits ayant 50% de diéthylcétone, avec formation simultanée de 20% de propionate de méthyle.

En faisant la réaction avec CO et des amines, la carboxylation des oléfines provoque la formation d'amides, et cette réaction est plus rapide que celle de conversion des oléfines, avec du CO et des alcools, en esters.

Comme la synthèse des aldéhydes par carbonilation des oléfines avec CO et H_2 se pratique déjà sur une grande échelle dans l'industrie, nous croyons que d'autres produits intéressants, esters, amides, cétones, alcools, peuvent également se former par synthèse d'oléfines et de CO, pourvu que la réaction soit conduite en présence d'alcools ou d'amines.

Introduction

Among the great number of applications suggested for olefins, one that is of particular interest is the synthesis of organic intermediates and (oxygenated) solvents which can be obtained by carbonylation and carboxylation with carbon oxide. The carbonylation reaction (oxo-synthesis) or production of aldehydes from olefins, CO and H_2 was discovered in 1938 (1) * by Dr Roehlen of the Ruhr-Chemie and was specially applied to the C_{12}-C_{18} olefins from Fischer's synthesis. As early as 1941 one of us had studied together with the Ruhr-Chemie and the Soc. Bombrini Parodi Delfino the application of this reaction to the lower olefins (C_2-C_4), particularly for the synthesis of propionic aldehyde from ethylene, CO and H_2 and its conversion by condensation, with formaldehyde, into methyl tri-methylolmethane. It was only after the war that some of his previous work on the kinetics of the oxo-synthesis (2) could be published.

The carboxylation of olefins, i.e. the introduction of a carboxylic group by reaction with CO and compounds containing mobile hydrogen which had already been dealt with before in an American paper, was later studied in detail by Reppe, who found that nickel-carbonyl especially in the presence of halogens, halides or free acids, was an extremely active catalyst for such reactions.

Continuing the investigations on the oxo-synthesis, which were started in our Institute almost 10 years ago (3), we recently examined the possibilities of using cobalt as a catalyst in the carboxylation and particularly in the synthesis of esters and substituted amides, and seeing that the first results obtained by the use of cyclo-hexene appeared to be promising, we have extended our investigations successively to ethylene, propylene and isobutylene. We shall summarize below the most interesting results which we have obtained in those experiments.

In our opinion the use of metallic cobalt as a catalyst in carboxylations, which was already attempted by Du Pont, Piganiol and Vialle (4), is quite promising, because cobalt, unlike nickel, allows of carrying out the synthesis of carboxylic derivatives (esters and amides) also in the absence of halogens or halides, so that in this way the corrosion of the apparatus can be avoided by the use of suitable metallic materials. This is due to the different chemical behaviour of cobalt and nickel. In a previous paper (5) we have explained how the activity of cobalt could be attributed to the possibility of its forming cobalt hydrocarbonyl and such complexes as are formed by activated adsorption of CO and H_2 on cobalt, which, as we have already seen in the case of the oxo-synthesis, must be considered as the real catalysts of the reaction. As is known, nickel from which no hydrocarbonyls exist, is active only in the presence of acids, halogens and halides, and it has been assumed that in such cases the real catalyst is an intermediate compound containing Ni, CO and halogens.

The high selectivity of the cobalt catalysts in the oxo-synthesis with respect to the formation of aldehydes has also been encountered in the synthesis of amides from olefins, CO and amines (6), whilst in the case of the synthesis of esters from olefins, CO and alcohols the selectivity is found to be much poorer, because in certain cases reactions parallel to carboxylation may prevail, such as the formation of aldehydes, alcohols and ketones.

I—Ester Synthesis

In previous experiments (4) carried out in the presence of very small quantities of catalyst, to which we refer for all details concerning the carboxylation we had examined the possible reaction mechanisms of the ester synthesis and its applicability both as regards the various types of olefinic products and alcohols used.

A series of systematic experiments starting from cyclohexene and primary, secondary and tertiary alcohols has enabled us to establish in this connection that the ester synthesis could be realized with the

* References given at end of paper.

primary and secondary alcohols, but not with the tertiary, which under the reaction conditions are dehydrated for the greater part to olefins.

The best yields were obtained when starting from primary alcohols, the most suitable of which was found to be methyl alcohol. On the strength of a close examination of the reaction products we have correlated this varying behaviour of the alcohols under our reaction conditions with their different dehydrogenatability. As a matter of fact, the quantities of olefins converted into aldehydes or acetals and alcohols by reaction with CO and hydrogen are smaller when operating in the presence of methyl alcohol, which is very difficult to dehydrogenate, and larger in the presence of secondary alcohols, which are dehydrogenated more easily. In the latter case the yield of esters is accordingly lower.

In Table I we show, for the sake of clarity the free energies of dehydrogenation for some alcohols used by us in the carboxylation of cyclo-hexene, as well as the mole ratios of the hexa-hydrobenzoic ester and the hexa-hydrobenzyl alcohol obtained.

TABLE I

Mole ratio $\frac{\textit{Hexa-hydrobenzoic ester}}{\textit{Hexa-hydrobenzyl alcohol}}$ *obtained in the carboxylation of cyclo-hexene in the presence of various alcohols*

Alcohols	Δ F of dehydrogenation at 498 K (in Kcals)	Mole ratio $\frac{\text{Hexa-hydrobenzoic ester}}{\text{Hexa-hydrobenzyl alcohol}}$
Methyl	+ 7.36	12.2
Ethyl	+ 3.06	0.67
n. Propyl	+ 2.94	0.76
Isopropyl	— 0.29	0.20

On the basis of the results obtained in the previous experiments on the carboxylation of cyclo-hexene we started the experiments on olefins with 2-4 carbon atoms, reacting propylene with carbon oxide and methyl alcohol. As catalyst we used cobalt on guhr or Raney cobalt; the best results were obtained with the latter catalyst used in considerable quantities at a temperature of 200° and a pressure of 300-400 atm. The alcohol/olefin and CO/olefin ratios used were:

$$\frac{CH_3\,OH}{C_3\,H_6} = 4.4 \text{ and } \frac{CO}{C_3H_6} = 4.3$$

Under the reaction conditions 86% by weight of the liquid reaction products obtained (i.e. excluding the gaseous or highly volatile products entrained with the gas) consisted of methyl butyrate (49%) and iso-butyrate (37%), whilst a large portion of the catalyst used was recovered apparently unchanged. The only secondary products available in appreciable quantities are butyric and isobutyric aldehydes and their dimethyl acetals.

As in the case of the oxo-synthesis with propylene, where the formation of n. butyric aldehyde prevails, in the ester synthesis a large quantity of methyl n. butyrate is recovered. This can be easily separated from the isobutyrate, because, unlike the latter, it does not form azeotropic mixtures with methanol, of which excess quantities are available in the reaction products.

In three experiments carried out with only slightly different $\frac{\text{alcohol}}{\text{propylene}}$ and $\frac{\text{CO}}{\text{propylene}}$ ratios the $\frac{\text{isobutyrate}}{\text{butyrate}}$ ratios are approximately 0.7.

As we had already noted in the case of the reaction between cyclo-hexene, carbon oxide and isopropyl alcohol, the decrease in the $\frac{\text{alcohol}}{\text{olefin}}$ ratio causes the formation of ketones and accordingly a reduction in the yield of esters. We are of opinion, however, that this reaction is also affected by the ratio between CO and olefins present in the liquid phase.

Approximately 80% of the methanol used was recovered from the liquid product.

The principal cause of a particular loss of methanol must be the formation of dimethyl ether. The methanol losses increase with the reaction time and, as in the case of the synthesis of acetic acid from methanol and CO, they may for the greater part be avoided by preventive addition of dimethyl ether.

The carboxylation of ethylene with CO and methanol takes place in a rather different way. In this case, too, the best results were obtained with the use of Raney cobalt at temperatures of 190-200° and pressures of 400-450 atm. The yields in esters were found to be somewhat lower, however, than those obtained with propylene; actually, the methyl propionate obtained represented approximately 37% of the total liquid reaction products, the remainder being formed for the greater part by di-ethyl ketone.

With isobutylene, the liquid products obtained besides methyl esters which could be theoretically expected (56%), also consisted of volatile products (15%) in addition to aldehyde products and a few high-boiling products (10%).

II—Direct synthesis of alcohols and ketones from olefins by reaction with CO

The poor selectivity shown by the cobalt catalysts in the ester synthesis has been used to explain the possible reactions between CO and olefins.

In preceding experiments on carboxylation of cyclohexene in the presence of alcohols we had pointed out that, though no hydrogen was used, the oxo-synthesis took place parallel to the reaction of the ester synthesis. Under the conditions used for the carboxylation in the presence of primary alcohols this leads to the formation of a mixture of hexa-hydrobenzoic aldehyde, of the corresponding acetals, and of alcohol originating from the reduction of the aldehyde, whereas in the presence of secondary alcohols it leads almost exclusively to the formation of hexa-hydrobenzyl alcohol.

In the oxo-synthesis which takes place parallel to the ester synthesis and which, particularly if secondary alcohols are used, strongly prevails over the latter, obviously use is made of the hydrogen formed as a result of the simultaneous dehydrogenation of the alcohol introduced; as we have already established, this is confirmed by the fact that this dehydrogenation is favoured according as the dehydrogenatability of the alcohol itself is greater. However, when operating under such temperature conditions that the equilibrium

$$R\text{-}CHOH\text{-}R_1 \rightleftarrows RCOR_1 + H_2$$

is almost on the left side, the hydrogen consumption for the oxo-reaction allows of continuing the dehydrogenation reaction.

It appears to be surprising, however, that in the oxo-synthesis carried out in the presence of large quantities of hydrogen, the principal products are aldehydes, whereas when operating in the presence of an easily dehydrogenatable alcohol, irrespective of the quantities of hydrogen available it is the alcohols that prevail.

The problem of direct production in one run of alcohols by oxo-synthesis according to Scheme I does not appear yet to be fully solved. In view of the advantages that might result from the direct production of alcohols,

$$R\text{-}CH = CH\text{-}R + CO + 2H_2 \rightarrow R\text{-}\underset{\displaystyle CH_2OH}{\underset{|}{CH}}\text{-}CH_2\text{-}R \qquad (1)$$

not only with respect to the economy of the process but also because in this way the aldehydic products are diluted and the bulk of the successive reactions can be avoided, we have started to study the reaction of oxo-synthesis in the presence of secondary alcohols. Although the experiments are not yet concluded, the results obtained appear to be encouraging in the case of cyclo-hexene; for example, when operating at a temperature of 200° and at pressures of 250-350 atm. with mixtures of CO and hydrogen 1 : 1 without secondary alcohols, the mole ratio $\frac{\text{hexa-hydrobenzyl alcohol}}{\text{hexa-hydrobenzoic aldehyde}}$ of the products obtained had a value of about 0.1; when operating under analogous conditions, but in the presence of an excess of isopropyl alcohol with respect to olefin, this ratio reached values of about 2.5. When substituting methyl alcohol for the isopropyl alcohol, the alcohol/aldehyde ratio decreases again to 0.31.

As regards propylene, when operating in the presence of isopropyl alcohol, under conditions analogous to those described for cyclo-hexene, the alcohol/aldehyde ratio in the reaction products shows a value of about 2.7, which tallies satisfactorily with the data found for cyclo-hexene.

The experiments further show that the production of acetone by dehydrogenation of isopropyl alcohol is not equal to that which can be foreseen according to the equation 2

$$R\text{-}CH = CH\text{-}R + CO + H_2 \rightarrow R\text{-}\underset{\displaystyle CHO}{\underset{|}{CH}}\text{-}CH_2\text{-}R$$

$$R\text{-}\underset{\displaystyle CHO}{\underset{|}{CH}}\text{–}CH_2\text{–}R + CH_3\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}CH_3 \rightarrow$$

$$\rightarrow R\text{–}\underset{\displaystyle CH_2OH}{\underset{|}{CH}}\text{–}CH_2\text{–}R + CH_3\ COCH_3. \quad . \quad . \quad (2)$$

and it is probable that analogous results will be obtained when small quantities of secondary alcohols are used.

Further experiments are being carried out in order to explain also from a theoretical point of view these new developments of the oxo-synthesis reaction.

When discussing the reaction between olefins, CO and alcohols, we have referred repeatedly to the presence of ketones in the reaction products.

Up to the present the formation of ketones according to the scheme set out under 3

$$2\ R\text{-}CH = CH\text{-}R + CO + H_2 \rightarrow R\text{-}CH_2\text{-}\underset{\displaystyle CO}{\underset{|}{CH}}\text{-}R \qquad (3)$$

$$R\text{-}CH_2\text{-}CH_2\text{-}R$$

$$R\text{-}CH = CH\text{-}R + CO + H_2 \rightarrow \underset{\displaystyle CHO}{\underset{|}{R\text{-}CH\text{-}CH_2\text{-}R}} \quad (4)$$

has been very little studied and the observations made on the subject are mostly limited to the case of ethylene with which this occurs most easily.

In a patent of DuPont (8) a description is given of a process based on the application of low pressures of CO according to which 22% of the ethylene reacted was found to be converted into diethyl ketone. If the reaction should take place entirely in the liquid phase, it would appear logical that a reduction of the quantity of CO in solution, i.e. of the $\frac{CO}{olefin}$ ratio, favours reaction 3 more than reaction 4.

Instead, our investigations into the ester synthesis have led us to establish how for the purpose of producing ketones, it is much more suitable to operate in the absence of gaseous hydrogen. The hydrogen required for the reaction may be supplied by dehydrogenation of alcohols or by conversion with CO of a small quantity of water contained in the initial products or formed in parallel reactions, e.g. dehydration of alcohols.

The best results have been obtained with ethylene at temperatures of 190-195° and pressures of about 400 atm. in the presence of methanol and an $\frac{alcohol}{olefin}$ ratio of 2.6 and a $\frac{CO}{olefin}$ ratio of 8.6, Raney cobalt being used as a catalyst.

Under these circumstances of the olefin reacted 53% was converted into diethyl ketone, whilst at the same time in parallel 20% was converted into methyl propionate and 7% into propionic aldehyde.

When isopropyl alcohol is substituted for methyl alcohol the ketone/ester ratio goes up considerably, but at the same time there is also an increase in the high boiling products which are difficult to identify.

In the case of the other olefins the formation of ketones appears to be encouraged to a smaller extent, thus in experiments carried out with propylene in the presence of methanol with a $\frac{CO}{C_3H_6}$ ratio of 1.16, a conversion into a C_7 ketone mixture was obtained corresponding to 27.5 % of the olefin intake and into esters of about 33 %.

III—Synthesis of substituted amides

Two different patents (9) filed during the late war by the I.G. revealed that acetylene and olefins react with CO, ammonia and primary and secondary amines so as to form amides of organic acids with one atom more than the olefin. As catalysts, nickel carbonyl used in stoichiometric quantities or a mixture of carbonyl nickel and nickel halogens or halides were recommended.

Moreover, it has been found that when operating in the presence of metals capable of forming hydrocarbonyls, of water and amines, amides with one carbon atom more than the starting olefin were obtained.

Continuing our investigations on the catalytic activity of cobalt in the carboxylation of olefins, we carried out various experiments (11), olefinic products being reacted with carbon oxide and aniline in the presence of metallic cobalt and in the absence of water.

When operating at temperatures of 180-220°, pressures of 300-500 atm. and an olefin/aniline ratio of about 1, the reaction proceeds at a speed equal to that of the oxo-synthesis, i.e. much higher than that of the ester synthesis, and the liquid reaction products consist for the greater part of anilides of the acids that could be expected according to Scheme 5.

$$\begin{array}{l} R \\ | \\ CH \\ \| \\ CH \\ | \\ R' \end{array} + CO + C_6H_5NH_2 \rightarrow \begin{array}{l} R \\ | \\ CH\text{-}CO\text{-}NH\text{-}C_6H_5 \\ | \\ CH_2 \\ | \\ R' \end{array} \quad (5)$$

$$\begin{array}{l} R \\ | \\ CH_2 \\ | \\ CH\text{-}CONH\ C_6H_5 \\ | \\ R' \end{array}$$

For example, when bringing about a reaction between ethylene with CO and aniline at a temperature of 220° and a pressure of 400 atm., the liquid and solid products obtained, less the unreacted aniline, were found to consist to the extent of about 80 % of anilide of propionic acid, whereas in the case of propylene, under analogous conditions a mixture of anilides of butyric and isobutyric acid was obtained representing 85 % of the reaction products.

In the case of isobutylene, the reaction products consisted for the greater part of amide of isovaleric acid, it having been impossible to isolate the amide of trimethyl acetic acid.

Of course, the reaction of the synthesis of the substituted amides is not limited merely to the case of aniline; it is also encountered with other than

aromatic amines, e.g. alcyclic and aliphatic amines.

Thus, when causing cyclo-hexene to react with α naphthyl amine and carbon oxide, we obtain the α naphthyl amide of hexa-hydrobenzoic acid as described in a preceding paper.

When substituting cyclohexyl amine for α naphthyl amine, we obtained satisfactory yields of cyclohexyl amide of hexahydrobenzoic acid, which has not yet been described (m.pt 164; C found: 74.68 %; H: 11.19%; N: 6.82%; calc. for $C_{13}H_{23}ON$: C: 74.62%; N: 11.0%; N: 6.7%); moreover, when operating in the presence of stearyl amine, we obtained the stearyl amide of hexa-hydrobenzoic acid, which was unknown as well (m. pt 89; N found 3.76%; calc. for $C_{25}H_{45}ON$: N 3.71%).

The cobalt used as a catalyst is recovered for the greater part by filtration, but part of it is lost at the discharge of the gas in which, as a rule, the presence of volatile products containing cobalt, probably hydrocarbonyl of cobalt, is ascertained.

The only secondary product repeatedly encountered in appreciable quantities in the experiments carried out with aniline is diphenyl urea, the presence of which, as we have stated before (10), could be correlated with the formation of the hydrocarbonyl of cobalt.

On the whole, the synthesis of anilides shows much analogy with the oxo-synthesis as far as catalysts and reaction speed are concerned and offers the advantage over the latter that the products obtained are much more uniform, which is essentially due to the great stability of the substituted amides under reaction conditions, which hardly allow of subsequent secondary reactions.

Conclusions

The short notes on the investigations which are now being carried out show how in spite of the tremendous work done by Roehlen, Reppe, and various American and English authors, the study of the reactions between olefins and CO may still yield unexpected results.

This is partly due to the fact that the present knowledge of the chemical properties of the carbonyl compounds of the metals of the iron group, which appears to be extremely interesting, is rather scanty. Among them we mention as particularly interesting the reactions between carbonyl cobalt and compounds containing hydrogen, with the formation of hydrocarbonyls of cobalt which are probably responsible for the catalytic action of cobalt in the reactions performed in the absence of hydrogen.

From an industrial point of view the ester synthesis reaction may be suitably limited to the preparation of methyl esters, which can be realized with satisfactory yields, whereas for the synthesis of esters of other alcohols the interchange of transester radicals between the methyl esters obtained by carboxylation and the desired alcohols is considered more suitable wherever possible.

Finally, of some interest for the preparation of oxygenated solvents would appear our experiments concerning the simultaneous synthesis of esters and ketones from ethylene and propylene, in which more than 80 % of the liquid products obtained is formed by di-ethyl ketone (b.p. 103) and by methyl propionate (b.p. 79.9), respectively, and by ketones C_7 and methyl butyrates and iso-butyrates, respectively.

The synthesis of the amides from olefins, CO and amines allows of obtaining in an easy manner and with high yields a wide range of compounds which, so far, had mainly been used only for laboratory preparation, but which can be applied on a much larger scale.

The amides most extensively used had actually been up till then the formamides, successfully applied as solvents. We assume that the characteristics of relative stability with respect to alkalis and acids at low temperature and the highly remarkable stability with regard to high temperatures of the amides generally will allow interesting applications of these amides. Moreover, the importance of this process should not be disregarded, e.g. organic acids can be easily obtained by saponification of the amides with aqueous inorganic acid at high temperatures with simultaneous recovery of the amines.

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(10) See (6).

DISCUSSION

This paper was discussed together with the paper by H. Hoog on "The Oxo-Process—Research, Development, and Product Application". See p. 20.

E. J. BRILL * PUBLISHER * LEIDEN (HOLLAND)

For the end of 1951 the appearance is scheduled of the complete

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