

3. The following heats of addition of 1 mole of hydrogen have been obtained at 302°K.

	ΔH in cal./mole.
1,4-Dihydronaphthalene	-27,121 \pm 101
1,2-Dihydronaphthalene	-24,098 \pm 199
Methyl <i>cis</i> -cinnamate	-28,190 \pm 238
Methyl <i>trans</i> -cinnamate	-24,183 \pm 102
<i>i</i> -Stilbene	-25,801 \pm 202
Stilbene	-20,136 \pm 36
Diethyl maleate	-33,519 \pm 153
Diethyl fumarate	-29,303 \pm 148
1,4-Diphenylbutadiene	-44,039 \pm 148

The values apply to the reactions X(liquid) + H₂(gas) \rightarrow Y(liquid), except in the case of 1,4-diphenylbutadiene, where the value applies to the reaction X(dissolved in glacial acetic acid) + H₂(gas) \rightarrow Y(dissolved in glacial acetic acid).

4. These results have been found to agree with the rules put forward by Kistiakowsky for the effect of substituents on the heat of hydrogenation of the ethylenic double bond.

5. Values have been obtained for the increase in stability, due to conjugation, of certain of the compounds investigated, and the heats of isomerization of the pairs of stereoisomers considered.

6. The heat of complete hydrogenation of 1,2-dihydronaphthalene has been shown to be greater than that for indene, the corresponding 5-membered-ring compound, in agreement with results previously obtained by Kistiakowsky and his co-workers for other similar pairs of compounds.

CAMBRIDGE, MASSACHUSETTS

RECEIVED JANUARY 29, 1942

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Studies in Gaseous Hydrogenation and Polymerization Reactions¹

BY HUGH D. BURNHAM² AND ROBERT N. PEASE

Earlier work from this and other laboratories has led to the now quite generally accepted conclusion that the decomposition of many organic compounds occurs in part, at least, through reactions of the chain type.³ One of the most effective methods of demonstrating the presence of reaction chains has been to observe the rate of decomposition in the presence and absence of small quantities of nitric oxide. Apparently nitric oxide is capable of reacting with the type of chain carriers found in pyrolysis of the paraffins, ethers and of some aldehydes⁴ so that a lower reaction rate in the presence of nitric oxide is taken to indicate that part of the reaction at least occurs by chain type processes.

Since the inhibition by nitric oxide must affect both the forward and reverse reactions to an equivalent degree (otherwise the position of equilibrium must necessarily shift), it was to be anticipated that the hydrogenation of ethylene as well as the decomposition of ethane ($C_2H_6 \rightleftharpoons H_2 + C_2H_4$) must be inhibited by nitric oxide. A

preliminary communication on this subject already has appeared.⁵ Further, it was believed that if the polymerization of ethylene could be inhibited to a greater extent than the hydrogenation reaction, then the hydrogenation could be studied over greater ethylene/hydrogen ratios than had heretofore been possible. Unfortunately, this has not been found to be the case, though polymerization is inhibited.

Experimental

Kinetic data were obtained from pressure measurements at constant volume, supplemented by analysis of residual gases. For the most part the apparatus was of a familiar type. The reaction bulb was a cylindrical Pyrex glass vessel 3.5 cm. in diameter and 22 cm. long. The method of mounting the bulb in the specially constructed furnace and the photoelectric thermostat control are the same as previously used in this Laboratory and described previously.⁶

Ethylene and propylene were obtained in commercial cylinders. The olefins were purified by repeated freezing out in liquid air and pumping off the residual gases. On warming up, the first portions were discarded and middle portions stored for experiments. Acetylene was obtained from a Prest-O-lite cylinder in which the gas is dissolved in acetone. The gas was passed through a calcium chloride tower. Subsequent purification was the same as that described for the olefins. Electrolytic hydrogen was further purified by passing over platinized asbestos at 300° and then through a liquid air trap to remove water.

(1) Abstracted from a thesis by Hugh D. Burnham, presented to the faculty of Princeton University, in partial fulfillment of the requirements for the Ph.D. degree, June, 1940.

(2) Present address, Wood River Research Laboratories, Shell Oil Company, Roxana, Illinois.

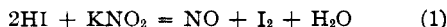
(3) Ethers: Staveley and Hinshelwood, *Proc. Roy. Soc. (London)*, **A159**, 192 (1937); Paraffins: Staveley, *ibid.*, **A162**, 557 (1937); Hobbs and Hinshelwood, *ibid.*, **A167**, 447 (1938); Echols and Pease, *THIS JOURNAL*, **61**, 1024 (1939).

(4) Staveley and Hinshelwood, *J. Chem. Soc.*, 1568 (1937).

(5) Burnham and Pease, *THIS JOURNAL*, **62**, 453 (1940).

(6) Echols and Pease, *ibid.*, **61**, 208 (1939).

The procedure for the preparation of nitric oxide was that recommended by Giauque and Johnston⁷ by the reaction



The purification consisted of scrubbing with concentrated potassium hydroxide solution followed by low temperature fractionation.

The reactants in the desired proportions were premixed by passage several times between two glass bulbs connected by a capillary to ensure homogeneity of the mixture before introduction into the reaction bulb. After the desired length of time in the furnace, or after the desired pressure change had occurred, the gases were expanded into the evacuated system and pumped into the gas sample buret. Reaction products were analyzed volumetrically. The amount of unreacted nitric oxide was determined by adding excess oxygen, absorbing the nitric oxide which was thus formed in potassium hydroxide solution, then removing the remainder of the oxygen by alkaline pyrogallol solution. Net decrease in volume was taken as nitric oxide. Olefins higher than ethylene were determined by absorption in 90% sulfuric acid and the ethylene was absorbed in the usual way in dilute bromine water. Since never more than a trace of acetylene had previously been reported in the pyrolysis of ethylene at the temperatures employed, it was not thought necessary to distinguish between these two hydrocarbons. Corrections were applied for the amount of ethylene dissolving in the sulfuric acid. If the analysis was that from an acetylene run, the acetylene was absorbed in the bromine water. In this case no separation from ethylene was required as previous work had shown that only very small quantities of ethylene, if any, were obtained from the pyrolysis of acetylene.

In the analysis of residual gases from runs with propylene, the butylenes were separated from propylene by selective absorption in 62.5% sulfuric acid as was done by Hurd and Meinert.⁸ This separation is admittedly rough. However, the procedure (including the time of contact between the gases and the acid) was standardized, and corrections determined on mixtures containing known amounts of propylene were applied for the amount of propylene dissolving in acid of this concentration.

The hydrogen was burned out by passing the gas sample over copper oxide at 300° until no further change in volume could be detected. The volume of the residual gas less the volume of nitrogen originally contained in the analytical system gave the amount of saturated hydrocarbons formed.

Polymerization of Ethylene.—The polymerization of ethylene was studied over the temperature range 400–525°. If the primary process were the dimerization of ethylene



and no complicating secondary reactions occurred, then the ratio of the amount of ethylene consumed to the observed pressure decrease should be exactly two. At the lowest temperature studied and at 10% reaction a value of 2.04 for this ratio was obtained. At 20% reaction at 400°, however, this increased to 2.30, and at 525° and 20% reaction the ratio was 2.81. The course of the reaction was therefore not accurately indicated by the pressure record.

For each set of initial conditions, a group of runs was made to various percentages of reaction. The amount of ethylene consumed as determined by analysis was then plotted against the time, a smooth curve being drawn through the several points. Since the pressure readings were made every few minutes during the course of the runs, the actual points are not shown on the curves showing pressure decrease as a function of time.

The course of the runs for both the normal polymerization of ethylene and the nitric oxide-inhibited polymerization at 500° are shown in Fig. 1. The initial induction period exhibited by all of the uninhibited reactions considerably complicates the kinetics of the polymerization. Previous authors have indicated that the reaction was bimolecular⁹ or between first and second order.¹⁰ The increase of the rate with per cent. reaction was attributed by Pease and also by Storch¹¹ to an acceleration by product.

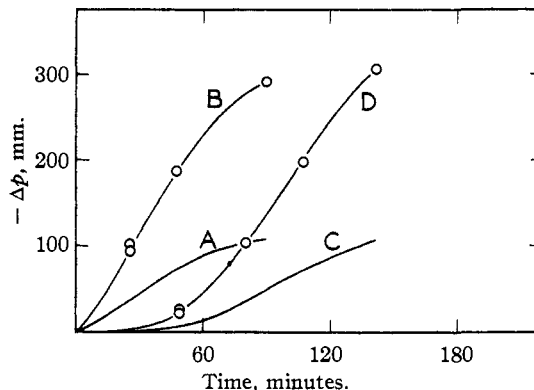


Fig. 1.—Polymerization of ethylene at 500°: A, pressure decrease, p_0 of $\text{C}_2\text{H}_4 = 713$ mm.; B, ethylene consumed in A; C, same as A with 10 mm. of nitric oxide; D, ethylene consumed in C.

An examination of Fig. 1 shows two facts of immediate interest. The nitric oxide cuts down the initial rate of the polymerization to an almost immeasurably small value. Secondly, the effect of nitric oxide is transient. There is a subsequent rise in rate and after about 10–20% reaction, the rate becomes equal to the normal rate of polymerization (or even a little greater). That the disappearance of the inhibition is not due to the complete loss of nitric oxide is shown by the data in Table I.

All the inhibited runs shown in Table I were reacting at about the normal polymerization rate for the uninhibited reaction at the time they were removed from the furnace. In other words, the

(7) Giauque and Johnston, *THIS JOURNAL*, **51**, 3201 (1929).

(8) Hurd and Meinert, *ibid.*, **52**, 4978 (1930).

(9) Pease, *ibid.*, **53**, 613 (1931).

(10) Burk, Baldwin and Whitacre, *Ind. Eng. Chem.*, **29**, 326 (1937).

(11) Storch, *THIS JOURNAL*, **56**, 374 (1934); **57**, 2598 (1935).

TABLE I
EFFECT OF NITRIC OXIDE ON POLYMERIZATION OF
ETHYLENE
Temperature, 500°; initial ethylene, 713 mm.; observed
pressure decrease, 36 mm.

Nitric oxide, mm.	Time in minutes	Ethylene consumed, mm.	Nitric oxide remaining, mm.
0	25	102	..
5	69	96	5
10	77.5	103	10
20	92.5	104	10
40	48.5	97	28

inhibition effect had almost entirely disappeared even though very appreciable quantities of nitric oxide remain, as shown in the last column. If an impurity were present in the ethylene whose accelerating action could be largely suppressed by the initial addition of only 5 mm. of nitric oxide, then the much larger quantities of nitric oxide which remained in those runs in which 10, 20, or 40 mm. of nitric oxide were originally added should continue to suppress the reaction. It may be noted that the amount of inhibition passes through a maximum at about 20 mm. of nitric oxide under the above conditions.

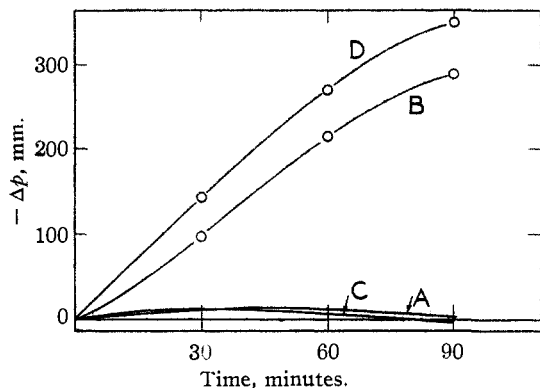


Fig. 2.—Polymerization of propylene at 500°: A, pressure decrease, p_0 of $C_3H_6 = 709$ mm.; B, propylene consumed in A; C, same as A with 20 mm. of nitric oxide; D, propylene consumed in C.

Polymerization of Propylene.—At the temperature at which this reaction was studied (500°) it is probably more correct to call the reaction a pyrolysis rather than a polymerization as the formation of very appreciable quantities of ethylene and saturated hydrocarbons was observed. The pressure record was found to have even less significance as an indication of the extent of the reaction than in the experiments with ethylene. At 500° and an initial pressure of 709 mm. of propylene, the pressure record actually passed through a minimum at around forty-five minutes

of reaction, even though the amount of propylene as shown by analysis continued to decrease. In Fig. 2 the propylene used and the actual pressure decrease are plotted against time. Comparison of Figs. 1 and 2 reveals a very striking difference between ethylene and propylene polymerizations in their behavior toward additions of nitric oxide. Not only does the nitric oxide eliminate the very slight induction period indicated by both the pressure record and the analyses for the normal polymerization of propylene, but apparently the nitric oxide has a positive catalytic effect on the rate of disappearance of propylene. At 500° and with an initial propylene pressure of 710 mm. and an initial nitric oxide pressure of 19 mm., it was found by analysis that 9 mm. of nitric oxide remained after 348 mm. of propylene had reacted.

A slight positive catalytic effect of an excess of nitric oxide over that required to produce maximum inhibition has been mentioned by previous authors¹² so that the effect described here may be due to the fact that the ratio of nitric oxide to propylene is too high. This is hardly likely in that a large amount of inhibition was obtained in the ethylene polymerization using 40 mm. of nitric oxide with 713 mm. of ethylene at 500°, and Echols and Pease³ obtained their maximum inhibition in the decomposition of normal butane using 40 mm. of nitric oxide with 200 mm. of the hydrocarbon at 520°.

Since the experiments on propylene were made subsequent to the experiments on ethylene, it was thought that possibly the nitric oxide had altered due to some impurity in the system. A further run on the polymerization of ethylene showed that this was not the case as the nitric oxide was capable of inhibiting the ethylene polymerization as much as was observed in the earlier runs.

In the work of Echols and Pease^{3,6} on the thermal decomposition of normal butane, it was reported that propylene was one of the products which could inhibit the decomposition. They state, however, that for small additions about twenty times as much propylene as nitric oxide was required to give the same amount of inhibition. Several runs were made to study the effect of initial propylene on the polymerization of ethylene; the results are shown in Table II.

It will be recalled from Table I that at the lowest concentration of nitric oxide used (5 mm.)

(12) Staveley and Hinshelwood, *Proc. Roy. Soc. (London)*, **A154**, 335 (1936).

TABLE II
EFFECT OF ADDED PROPYLENE ON THE POLYMERIZATION OF
ETHYLENE AT 500°

Initial pressure, mm. Ethyl-ene	Propyl-ene	Press. decr., mm.	Time in minutes	Ethyl-ene con- sumed, mm.	Higher olefins, mm.	Apparent propylene recov., mm.
713	0	36	25	102	53	..
712	0	36	24.5	94	54	..
713	20	37	25.5	93	71	17
713	40	36	24.5	95	88	34

considerable inhibition of ethylene polymerization under conditions similar to the above was obtained so that had the propylene been even one-twentieth as effective as nitric oxide, some inhibition should have been observed. From the data of Table II it may be stated that within the experimental error of the method propylene in the amounts used above does not inhibit the polymerization of ethylene.

Polymerization of Acetylene.—The reaction of acetylene with itself is not as complicated by secondary reactions forming products other than the solid or liquid polymers as is the polymerization of ethylene and propylene. On withdrawal from the reaction vessel in the furnace a condensation to liquid and/or solid polymers occurred but the analysis of the residual gases showed no gaseous polymer, saturated hydrocarbon or hydrogen. The effect of nitric oxide on the polymerization of acetylene is shown in Table III.

TABLE III
EFFECT OF NITRIC OXIDE ON POLYMERIZATION OF ACETYLENE AT 400°

Initial acetylene, mm.	Initial nitric oxide, mm.	Time in minutes	Pressure decrease, mm.	Acetylene consumed, mm.
711	0	114	72.5	93.0
711	0	108	73	93.5
711	20	1060	72	78

It will be seen that acetylene polymerization is greatly inhibited by nitric oxide. The amount of inhibition is greater with acetylene at 400° than with ethylene at 400° (data not shown). For acetylene the ratio of times to about 11% loss of acetylene with and without nitric oxide was approximately 12 while for ethylene this ratio was less than 4.

Analysis of the residual gases in that experiment in which nitric oxide was used (the rate of the inhibited reaction had increased to the normal rate at the same percentage of reaction by the time the gases were removed from the furnace) showed the absence of both nitric oxide and nitrogen so that the nitric oxide must have been incorporated

in the solid and liquid polymers formed. A fairly distinct break in the pressure record for the inhibited reaction occurred at around 1000 minutes, at which time the total pressure decrease was only about 40 mm. If this break marked the consumption of the initial addition of nitric oxide, and the main part of the acetylene used up at this point represents reaction with nitric oxide in the ratio of one molecule of acetylene to one molecule of nitric oxide, then the amount of acetylene actually polymerized in the first 1000 minutes would be very much less than that indicated by the data in the above table.

The complete disappearance of nitric oxide by reaction with the acetylene is similar to its behavior with dimethyl ether³ and is in contrast with its behavior toward the higher ethers and toward ethylene and propylene as mentioned in the previous sections.

Hydrogenation of Ethylene.—Inhibition of the hydrogenation reaction by nitric oxide was to be anticipated in view of the fact that the decomposition of ethane to yield hydrogen and ethylene was subject to inhibition.³ From the work on the induced hydrogenation and polymerization of ethylene as well as the thermal reactions it is quite apparent¹³ that the hydrogenation reaction is closely coupled with that of polymerization. Its rate is of the same order of magnitude and in the presence of hydrogen the ethylene which would have polymerized is largely converted to ethane. On the other hand, it was hoped at the start of the work that perhaps conditions could be found under which the polymerization of ethylene was considerably more inhibited than the hydrogenation. It would then be possible, by making small additions of nitric oxide, to study the kinetics of the hydrogenation reaction over a much wider range of hydrogen-ethylene ratios than had previously been possible, perhaps even in ethylene-rich mixtures. Unfortunately, this could not be realized under any of the conditions studied in the present work.

Hydrogenation experiments were carried out at 500° with and without the addition of nitric oxide, using hydrogen-ethylene ratios of 3:1, 2:1, 1:2 and 1:4. In addition, some experiments were made at 550° with a hydrogen-ethylene ratio of 3:1. The data for the mixture utilizing a hydrogen-ethylene ratio of 2:1 are shown in Figure 3.

At 500° and with the hydrogen-rich mixtures,

(13) Pease, THIS JOURNAL, 52, 1156 (1930).

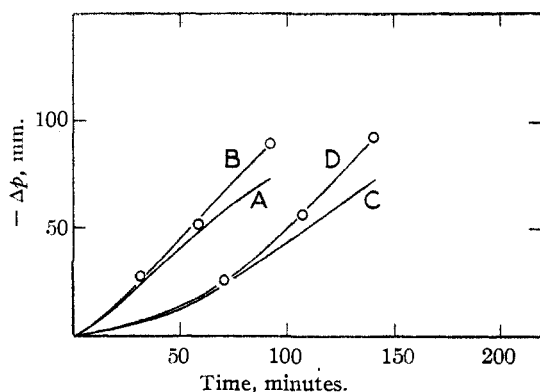
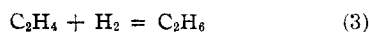


Fig. 3.—Hydrogenation of ethylene at 500°: A, pressure decrease, p_0 of $C_2H_4 = 237$ mm., p_0 of $H_2 = 477$ mm.; B, ethylene consumed in A; C, same as A with 20 mm. of nitric oxide; D, ethylene consumed in C.

no polymers either gaseous or liquid were found, but it was evident from the analyses that more ethylene was consumed than corresponded to the pressure change if the only reaction to be expected were



The fact that the ratio of ethylene consumed to pressure decrease was greater than unity was ascribed to a slight amount of ethylene undergoing polymerization, the products of which were subsequently hydrogenated and hence escaped detection as higher olefins. The amount of such simultaneous polymerization increased with the ratio of ethylene to hydrogen in the reacting mixture.

The amount of inhibition decreased markedly with the amount of ethylene in the initial reaction mixture. However, even in the hydrogen-rich mixture of 3:1 where it was shown by analysis that 90 to 95% of the ethylene is hydrogenated directly to ethane, the effect of inhibition remained measurable so that the inhibition of the consumption of ethylene must be due in part at least to the inhibition of the hydrogenation reaction.

As in the case of the polymerization of ethylene, the effect of the additions of nitric oxide is transient. The rate is again immeasurably slow at first but increases so that after about 10% reaction it is approximately equal to the normal rate of reaction at the same percentage of ethylene consumption. That the increase in rate is not due to the simultaneous disappearance of nitric oxide was shown by the analyses. In no case was the amount of nitric oxide consumed more than 50% of that initially added.

The existence of the inhibition effect and argu-

ments similar to those presented in the preceding section on ethylene polymerization indicate that the hydrogenation of ethylene as well as the polymerization of ethylene may be a chain reaction.

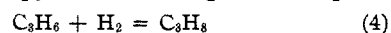
The experiments at 550° were made to determine the effect of temperature on the amount of inhibition obtained. The results are compiled in Table IV along with similar data at 500° for the same initial conditions and percentage reaction.

TABLE IV
EFFECT OF TEMPERATURE ON THE AMOUNT OF INHIBITION IN THE HYDROGENATION OF ETHYLENE

Temp., °C.	Initial ethylene, mm.	Initial hydrogen, mm.	Nitric oxide, mm.	Fraction ethylene consumed	Time in minutes
500	178	537	0	0.12	32
500	178	537	20	.12	43
550	177	538.5	0	.12	5.9
550	177	536.5	21	.12	13.5

These values differ slightly from the preliminary communication,¹⁴ due to a recalculation of the analytical data. It is apparent, as previously pointed out, that the effect of nitric oxide on the hydrogenation reaction increases with the temperature. This suggested the use of nitric oxide to inhibit the polymerization of ethylene while the hydrogenation process is studied in ethylene-rich mixtures. The difficulty is, however, that at lower temperatures where the initial effect of nitric oxide on the hydrogenation of ethylene is relatively less than on the polymerization of ethylene, the transient effect of the nitric oxide is over before any great amount of ethylene and hydrogen can react.

Hydrogenation of Propylene.—Experiments on the hydrogenation of propylene were carried out at 500° using hydrogen-propylene ratios of 1:2 and 2:1. Even in the hydrogen-rich mixture not only was there a large discrepancy between the pressure decrease and the actual amount of propylene consumed, but the amount of hydrogen used was considerably less than the amount of propylene used. Hence the combination of hydrogen and propylene according to the equation



does not represent a very big fraction of the amount of reaction. A large amount of reaction yielding no pressure change—such as the hydrogenation of propylene to give methane and ethylene—will account for the results and at the same time account for the substantial quantities of these last two gases always obtained.

(14) Burnham and Pease, *THIS JOURNAL*, **62**, 453 (1940).

The data for the experiments with a hydrogen-propylene ratio of 2:1 were treated in the same manner as described in the previous sections and are presented in Fig. 4. Again the striking feature found in the figure is that the addition of nitric oxide causes an acceleration in the rate of propylene consumption. The effect of the nitric oxide seems to be mainly due to the elimination of the small induction period which is indicated by the pressure record in those experiments in which propylene and hydrogen alone were used.

Discussion

The inhibition by nitric oxide has been ascribed by many authors^{8,15} as due to the property of nitric oxide of uniting with the chain carrying radicals or atoms. The subsequent history of the molecules so generated would be difficult to trace. Presumably, such compounds should be particularly labile at the temperature at which the reactions were studied, and according to the analyses some of the nitric oxide was used up. (All of the nitric oxide was consumed in the polymerization of acetylene so that the discussion to follow does not apply to this particular case.)

In the case of the polymerization and hydrogenation of ethylene, the fact that the inhibition was transient without the complete loss of nitric oxide indicates that the remaining nitric oxide is not capable of removing chain carriers. After the inhibition period is over, the rate increases until at about 10–20% reaction it is practically equal to that of the normal reaction at the same percentage conversion. The attainment of such a rate in the presence of the still fairly large amounts of nitric oxide remaining means that the nitric oxide is "saturated" with respect to the radicals and that "feed back" is occurring. It must therefore be assumed, as was suggested by Echols and Pease⁸ to explain similar results on the decomposition of normal butane, that an equilibrium exists between the free radicals and the nitric oxide molecules



where R is methyl, ethyl or perhaps H atom.

Within the error of the experimental method the polymerization of ethylene was not inhibited by propylene. The action of free radicals, which have just been shown to exist in the polymerization of ethylene, on the added propylene would

(15) Staveley and Hinshelwood, *Trans. Faraday Soc.*, **35**, 845 (1939).

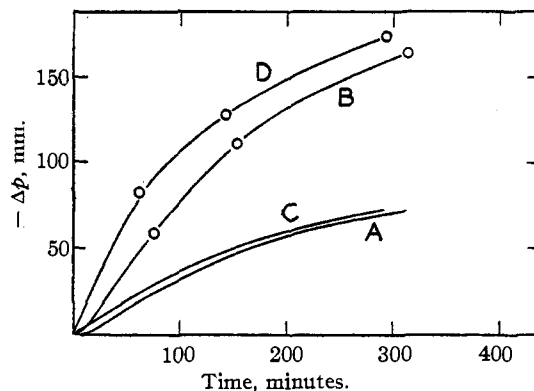
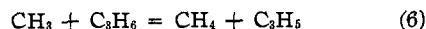


Fig. 4.—Hydrogenation of propylene at 500°: A, pressure decrease, p_0 of $C_3H_6 = 235$ mm., $p_0 = 477$ mm.; B, propylene consumed in A; C, same as A with 20 mm. of nitric oxide; propylene consumed in C.

most certainly yield allyl radicals plus a saturated hydrocarbon



That such a reaction takes place more readily than the corresponding reaction of the methyl radical with saturated hydrocarbons or ethylene is shown by experiments of Smith and Taylor,¹⁶ from which the energies of activation for the formation of methane by the interaction of methyl radicals with various hydrocarbons were obtained. For the above reaction these authors report an activation energy of 3.1 kcal., which is the lowest found in the whole range of hydrocarbons studied. They interpret this result as being associated with the resonance characteristics of the allyl radical. It has been estimated that the resonance energy of the allyl radical amounts to 15.4 kcal.¹⁷

The formation of allyl in the chain decomposition process of a saturated hydrocarbon would be an inefficient chain-carrying step as the longer lifetime and lesser reactivity of the allyl radical would allow it a greater chance to disappear by collision with itself or with another radical to produce diallyl or a substituted propylene, respectively. The inhibition of the butane decomposition by propylene as found by Echols and Pease, which, however, has only one-twentieth to one-thirtieth the inhibiting ability of nitric oxide, is thus explained. The fact that propylene does not inhibit the ethylene polymerization indicates that the association of ethylene with allyl radicals to form a higher allyl radical must

(16) Taylor and Smith, *J. Chem. Physics*, **8**, 543 (1940); cf. Beeck and Rust, *ibid.*, **9**, 480 (1941).

(17) Lennard-Jones and Coulson, *Trans. Faraday Soc.*, **35**, 811 (1939).

be just as probable as the association of ethylene with alkyl radicals to generate a higher alkyl radical. It is not at all unlikely that the reaction of allyl radical with an olefin to produce the higher allyl radical results in little or no loss of resonance.

Summary

It has been found that the polymerization reactions of ethylene and of acetylene and the hydrogenation reaction of ethylene are inhibited by small initial additions of nitric oxide. The results have been interpreted as indicating a chain mechanism for the above reactions, and that the nitric oxide acts by combining with the free radicals or atoms and effectively prevents

their further participation in the chain reaction.

The polymerization and hydrogenation reactions of propylene were found not to be inhibited by small additions of nitric oxide. On the contrary, a slight acceleration of these reactions is caused by the addition of nitric oxide. Although no explanation for this is offered, it is pointed out that this is only one of the instances in which the reactions of ethylene differ in wide respects from the corresponding reactions of its next higher homolog, propylene. The catalytic effect of nitric oxide neither favors nor denies the possibility of a chain mechanism in the propylene reactions studied.

PRINCETON, N. J.

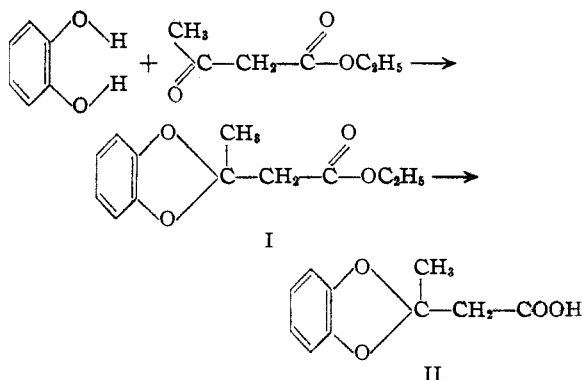
RECEIVED FEBRUARY 2, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Base-catalyzed Cleavage of Methylenedioxy Rings

BY RICHARD T. ARNOLD, NEWMAN BORTNICK AND ENOS McMULLEN

Catechol reacts with acetoacetic ester in the presence of phosphorus pentoxide to form 2-methyl-2-carbomethoxymethyl-1,3-benzodioxole (I).¹ This ester is reported to undergo hydrolysis leading to an acid (II) which melts at 61° although no directions were given in the original paper.

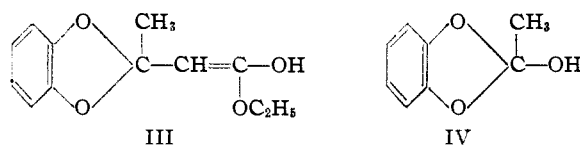


In another connection, a relatively large quantity of the acid (II) was required, and it was proposed to prepare it by the hydrolysis of I. Basic saponification of I followed by careful acidification of the reaction mixture gave the acid described by Slooff, but the yields were poor and the acid was accompanied by considerable quantities of catechol. It has been demonstrated repeatedly that simple methylenedioxy compounds, in agreement with their acetal (or ketal) structure, are

(1) Slooff, *Rec. trav. chim.*, **54**, 995 (1935).

stable toward bases. Thus Späth and Quietensky² have shown that dihydrosafrole is scarcely attacked by sodium ethoxide at 175° or by sodium hydroxide at 200°, and there are numerous other examples of this sort to be found in the literature. The surprisingly easy cleavage of the methylenedioxy ring system when I is hydrolyzed is an exception to the general behavior of these compounds, and it seemed likely that this is due to the relative position of the ester grouping to the ketal carbon atom.

A consideration of the formula III of the enol of I shows that this enol is a first vinylog³ of a partially hydrolyzed ortho ester IV



One substance of the type IV is known; it (V) is formed when an equimolecular mixture of benzaldehyde and phenanthraquinone is subjected to the action of ultraviolet light.⁴ When V is hydrolyzed, there is formed an alkali soluble material which yields phenanthraquinone on mild oxidation. These transformations are shown below.

(2) Späth and Quietensky, *Ber.*, **60**, 1882 (1927).

(3) Fuson, *Chem. Rev.*, **16**, 1 (1935).

(4) Schönberg and Moubacher, *J. Chem. Soc.*, 1430 (1939).