

THERMAL DECOMPOSITION OF ACETALDEHYDE IN THE PRESENCE OF NITRIC OXIDE

By

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The pyrolysis of acetaldehyde in the presence of nitric oxide has been studied in the temperature range 495–550 °C at an initial acetaldehyde pressure of 25–200 torr and at 0–50 torr nitric oxide pressure. The decomposition was followed by pressure measurements and by GC analysis. The order of reaction with respect to CH_3CHO and NO was determined by different methods. From pressure measurement data "influencing curves" were deduced and on this basis, some properties of the catalytic and inhibition region are summarized. Arrhenius parameters are given for the overall decomposition in the catalytic region. The effect of nitric oxide on the formation of major and some of the minor products (*e.g.* H_2 , C_2H_6 , C_2H_4 , acetone, HCN) was investigated in the catalytic and inhibited regions. The possible routes of product formation are shortly discussed and a simple mechanism is given for the NO influenced aldehyde decomposition.

Introduction

The influence on the acetaldehyde decomposition of different substances has been a frequently studied field of reaction kinetics. It was established that N_2O , H_2S , I_2 , Br_2 , O_2 , HCl , HBr , propylene, nitric oxide, etc. have a strong catalytic effect on the decomposition of acetaldehyde, while in the case of nitric oxide and propylene, inhibition takes place, too [1, 31–34]. In consequence of this double effect, the NO aroused considerable interest.

Many articles have been published in this field, the earlier ones, based on pressure measurements, did not provide detailed information [2, 3–5]. More recent investigations were carried out by gas chromatography (GC) and mass spectroscopy (MS) [6, 7]. These latest publications, altogether with LAIDLER's recent investigations [8, 9] give us nowadays the best informations in this field, stating the following: the order of decomposition with respect to acetaldehyde is $3/2$ in a wide pressure range of aldehyde and NO , and in the catalytic region the decomposition is proportional to the square root of NO concentration. SCHUCHMANN and LAIDLER [9] during the pyrolysis have indentified the products listed in Table I. Rates of formation of the most important products as a function of NO pressure are shown according to [9], in Fig. 1.

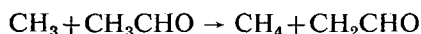
On the basis of the mentioned experimental results, LAIDLER assumes two chain carriers in the system, namely CH_3 and CH_2CHO radicals. The concentrations of these two chain carriers are independent of each other, and the NO influences

Table 1

Products of pyrolysis in the presence of NO according to SCHUCHMANN and LAIDLER [9]

Major products	Minor products	N ₂ -containing products	Compounds, which were not obtained during pyrolysis
CO	H ₂ , CO ₂ , H ₂ O, C ₂ H ₅ CHO, C ₂ H ₄	N ₂ , N ₂ O, HCN, CH ₃ NCO, C ₂ H ₅ NCO	CH ₂ O, CH ₃ ONO, CH ₃ NO ₂ , CH ₃ ONO ₂ , CH ₃ OH, CH ₃ CO, CH ₃ CN, C ₂ H ₅ OH, CH ₃ OC ₂ H ₅ , (CH ₃) ₂ CHOH, CH ₃ COCOCH ₃
CH ₄	C ₂ H ₆ , C ₃ H ₆ CH ₃ COCH ₃ CH ₃ COOCH = CH ₂ (crotonaldehyde)?		

their concentrations in different ways. In the case of methyl radicals, both generation and removal take place in a direct reaction with NO, while in the case of CH₂CHO radicals, the formation takes place in an indirect way



and the consumption of this radical commences in a direct reaction with NO.

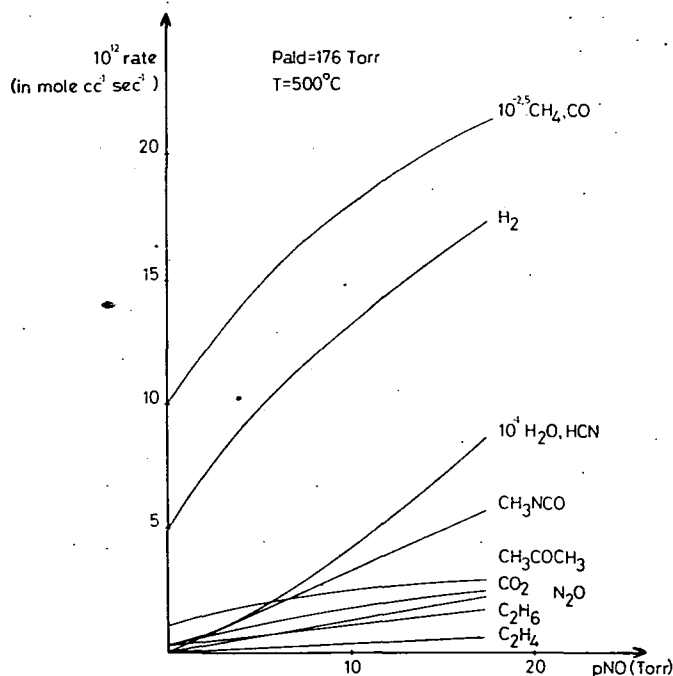
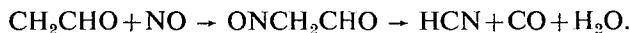


Fig. 1. Rate of formation of pyrolysis products as function of NO pressure, according to SCHUCHMANN and LAIDLER [9]. $p_{\text{ald}} = 176$ torr, $t = 500^\circ\text{C}$

LAIDLER assumes new initiation steps in the presence of NO, which explain the increase in the amount of major products. According to their very detailed analytical investigations SCHUCHMANN and LAIDLER proposed a more accurate mechanism consisting of 41 steps. The steady-state equations derived from this mechanism are in good agreement with the experimental rate—[NO] curves, which verifies the validity of the mechanism.

After finishing the investigation of the decomposition of the pure acetaldehyde [25], we wished to clear up the influence of NO on the kinetics of decomposition and the distribution of products. Detailed investigations had been carried out earlier in our Institute with the propionaldehyde—NO system [10, 11], which offered a good opportunity to compare these two systems.

Experimental

The apparatus and procedures were essentially the same as used previously [25]. The mixture of aldehyde and NO was left to stand half an hour, during which, to promote good mixing, we used thermodiffusional stirring. This time was enough to reach a good mixing, and the "cold reaction", mentioned by SCHUCHMANN and LAIDLER [9], (*i.e.* the reaction between aldehyde and NO at room temperature and in darkness) could not be observed. In most cases the reaction was followed by the measurement of pressure change and the products were analysed by GC. To facilitate the analysis, the products were separated into fractions condensable and non condensable at liquid air temperature. The GC apparatus used and the methods of analysis were similar to those used previously [25].

Materials. NO was produced by the method of WINKLER [12]. The frozen NO was subjected to low temperature bulb to bulb distillation and was stored in a storage vessel.

CH₃CHO. The purification and storage of acetaldehyde were the same as described earlier [25]. In the same paper we gave detailed methods of purification of the chemicals used to calibrate the GC.

Pressure—time measurements

The experiments were carried out at five temperatures (495.5, 512, 527.5, 539.5, 550.5 °C) and at four different aldehyde concentrations (25, 50, 100, 200 torr). The concentration of NO changed between 0 and 50 torr. The reproducibility of our experiments was satisfactory. The character of pressure—time curves, plotted from the experimental data, does not change in the presence of NO, as it can be seen in Fig. 2; only, depending on the effect of NO, a rate increase is observable.

The order of reaction

The order of reaction with respect to aldehyde has been found to be 3/2 in a wide pressure range [7]. From the initial rates (calculated from the pressure—time curves by computer), the order of reaction with respect of aldehyde was determined and agreement with literature was found, but only in the case when the aldehyde

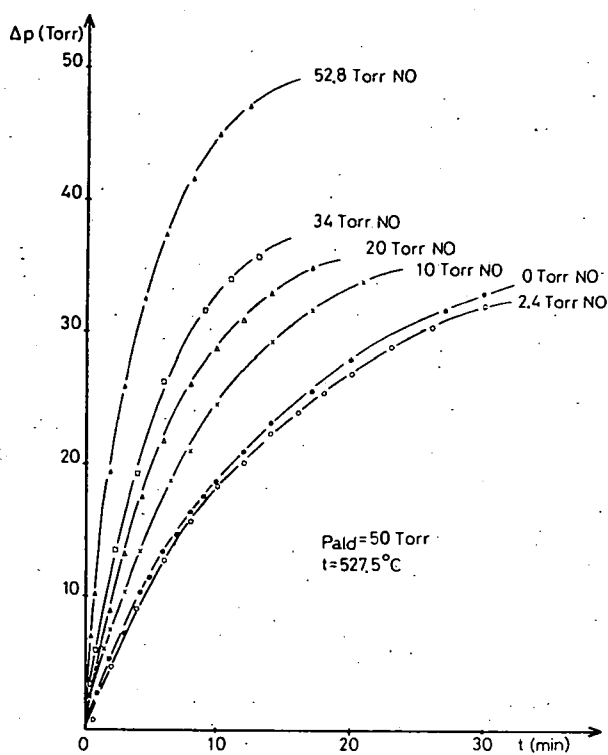


Fig. 2. Pressure—time curves at different NO concentrations. \bullet 0 torr; \circ 2.4 torr; \times 10 torr; Δ 20 torr; \square 34 torr; \blacktriangle 52.8 torr NO. $p_{ald} = 50$ torr, $t = 527.5^\circ\text{C}$

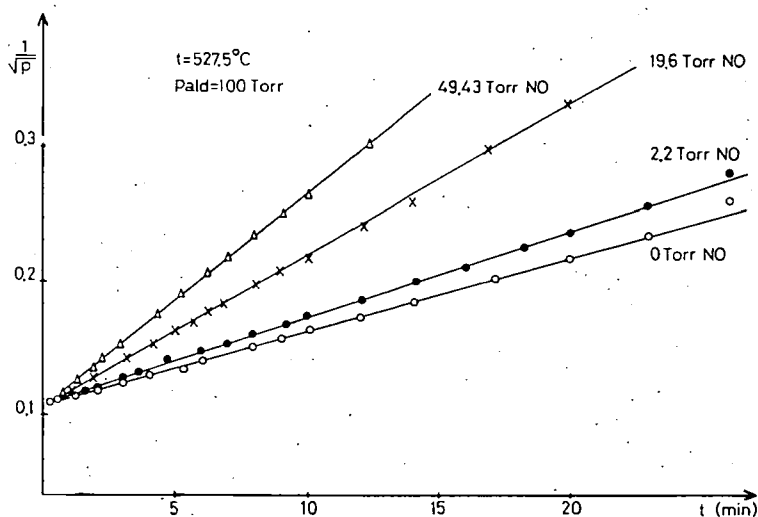


Fig. 3. $p^{-1/2}$ - t curves at different NO concentrations. $t = 527.5^\circ\text{C}$, $p_{ald} = 100$ torr. \circ 0 torr; \bullet 2.2 torr; \times 19.6 torr; Δ 49.43 torr NO

concentration was above 50 torr and the NO concentration above 5 torr (*i.e.* in the so called catalytic region). This order did not show any significant change neither by the effect of temperature increase, nor due to the increase of NO concentration. This value and the same behaviour was found to be valid if the rate was calculated point by point from the pressure—time curves.

To check the validity of the above value of reaction order, the inverse square root of the actual pressure *vs.* time was plotted. This must give a straight line if the order of reaction is 3/2. As it can be seen from Fig. 3, this condition is fulfilled above 100 torr initial aldehyde concentration at any NO concentration, but at 50 and 25 torr aldehyde pressures a slight curvature can be observed.

Using the $\log w_0 - \log p_0$ graphs the order of reaction was determined with respect of NO concentration.

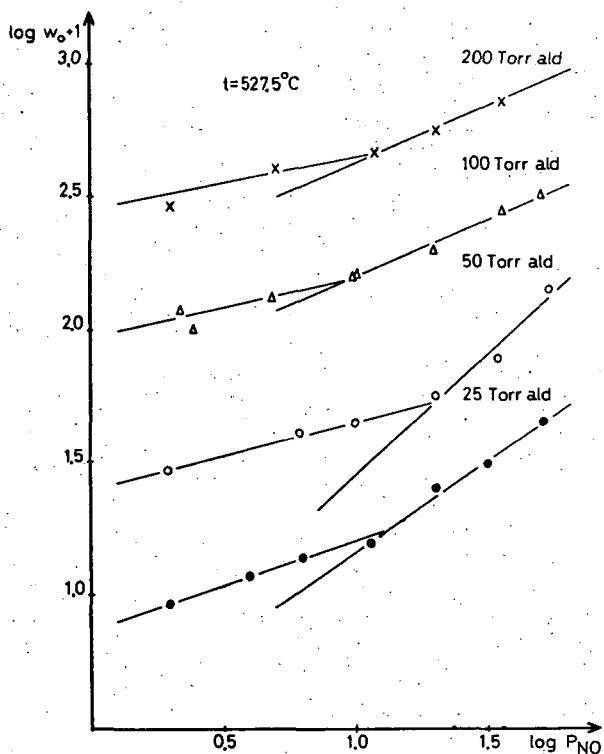


Fig. 4. $\log w_0 - \log p_0^{NO}$ curves at different aldehyde concentrations. $t = 527.5^\circ\text{C}$. ● 25 torr; ○ 50 torr; Δ 100 torr; × 200 torr aldehyde

As it can be seen from Fig. 4, where the results of a series of experiments are plotted, the experimental points under 5 torr NO always deviate consequently and a break appears in the line. Omitting these values, the order of decomposition with respect of NO will be very close to 0.5, which agrees quite well with the value found in literature.

As it was mentioned above, the order with respect to aldehyde in the presence of NO, under special circumstances ($p_{\text{ald}} > 50$ torr and $p_{\text{NO}} > 5$ torr) was found to be $3/2$, similarly to the decomposition of pure acetaldehyde, and on the basis of these data obtained by pressure measurements, $3/2$ order rate constants (k') were calculated. As the values of these rate constants showed no trend within one experiment; this means that the right order has been established. The mean values of the rate constants collected in Table II were used for the calculations. As it can be seen from the table, the rate constants change with increasing NO concentration.

On the basis of our experimental data the validity of the expression

$$x^{-1/2} = 1 + \frac{1}{2} k\tau$$

was checked.

Table II

$3/2$ Order rate constants, $k' \cdot 10^{-2}$ (in $l^{1/2} \text{ mole}^{-1} \text{ sec}^{-1}$) calculated from pressure—time measurements at different temperatures and at different initial aldehyde and NO pressures

t °C	P_{NO} (torr) \diagdown	0.5	1	10	20	35	50
	P_{ald} (torr)						
512 °C	25	2.0466	2.2842	3.3214	4.3910	6.2307	7.8356
	50	2.0061	2.0780	3.5765	4.9359	5.7482	6.4391
	100	2.2864	2.4938	3.3433	5.0071	6.1949	7.6908
	200	2.5683	2.8815	3.8727	—	6.4220	7.4857
527.5 °C	25	4.1725	3.0955	5.6788	7.9451	9.9824	13.0743
	50	4.0180	4.0552	5.7085	7.1422	9.4212	12.6311
	100	4.5319	4.5650	6.5204	8.1801	10.3819	12.0651
	200	—	—	7.0976	8.4977	10.4713	—
539.5 °C	25	5.6820	6.4810	7.9751	10.5422	17.9280	18.9714
	50	5.8059	6.0799	8.7783	10.9755	13.9311	17.4890
	100	6.4289	—	9.1310	11.9646	15.4762	18.2058
550.5 °C	25	8.7468	9.8916	13.3774	17.0703	22.3297	—
	50	9.0301	7.8097	12.2757	15.9104	19.9267	23.1799

This expression is obtained from

$$k = \frac{2}{t} [c^{-1/2} - c_0^{-1/2}]$$

by rearranging and introducing some symbols ($c/c_0 = x$ and $c_0^{1/2}t = \tau$).

In the case of reactions of $3/2$ order, plotting $x^{-1/2}$ against τ , a straight line is obtained, the slope of which gives $k/2$. This expression was found to be valid only in the catalytic region, as Fig. 5 shows.

On the basis of this expression, $3/2$ order rate constants were calculated from our experimental data.

Influencing curves

If k'_{NO} (the rate constant calculated from experiments in the presence of NO) is divided by k (rate constant' in the absence of NO), and k'_{NO}/k ($F(I)$) is plotted as a function of the pressure of NO, the curves obtained very characteristically show the inhibition and catalysis phenomena and offer the possibility of a quick view of experimental data. Typical influencing curves are shown in Fig. 6.

In Fig. 6, the points of the curves below and above the value 1 indicate inhibition and catalysis, respectively.

It can be seen from Fig. 6 that above 100 torr aldehyde concentration the rate of reaction monotonously increases with NO concentration (catalytic region). As seen from Fig. 6, above 150 torr aldehyde concentrations the effect of NO practically does not depend on the initial aldehyde concentration. This is proved by the fact that the experimental points at 150 and 200 torr aldehyde concentrations coincide with each other. The aldehyde dependence of the NO effect below 50 torr aldehyde appears not only in the decrease of catalytic effect, but also in inhibition. With increasing NO concentration the inhibition changes into catalysis.

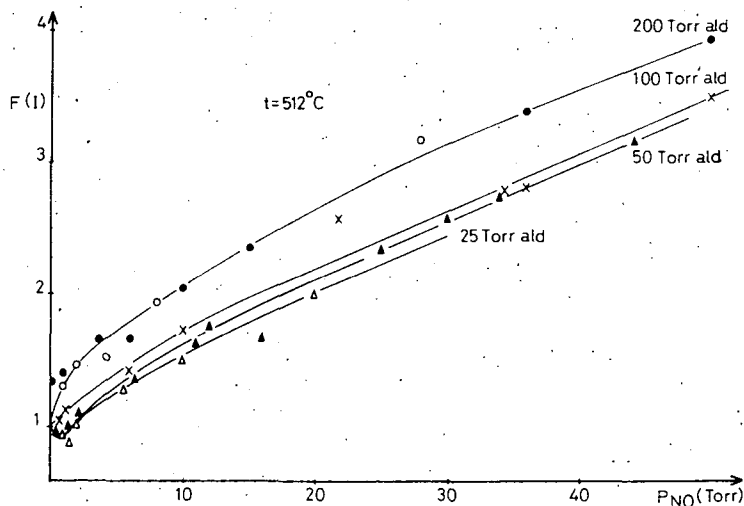


Fig. 6. Aldehyde dependence of influencing curves at 512°C. Δ 25 torr; \blacktriangle 50 torr; \times 100 torr; \circ 150 torr; \bullet 200 torr aldehyde

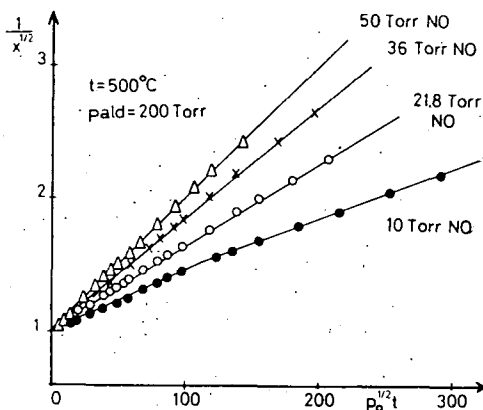


Fig. 5. $x^{-1/2} - p_0^{1/2} t$ (τ) relationship at different NO concentrations. $t = 500^\circ\text{C}$ $p_{\text{ald}} = 200$ torr. \bullet 10 torr; \circ 21.8 torr; \times 36 torr; Δ 50 torr NO

Similar behaviour was found by LAIDLER and EUSUF [13] in the case of propionaldehyde, where, independently from the initial aldehyde concentration, an inhibition period going over into catalysis was always found to appear. In the catalytic region the rate of reaction is independent of the pressure of aldehyde.

With increasing temperature, the degree of catalysis strongly decreases, as it can be seen from Fig. 7.

This decrease is very significant at higher concentrations of NO and aldehyde.

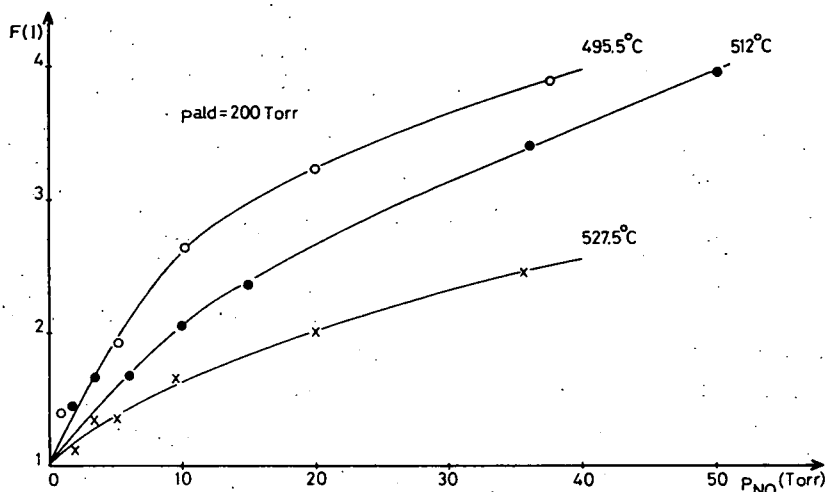


Fig. 7. Temperature dependence of influencing curves in the catalytic region.
 $p_{ald} = 200$ torr. ○ 495.5°C; ● 512°C; × 527.5°C

In contrary, by increasing the temperature, the inhibition markedly increases (Fig. 8).

It turns out from the influencing curves that the aldehyde decomposition in the presence of NO may be divided into two sections, *i.e.* the catalytic and inhibition sections. The characteristic features of these two stages can be summarized as follows.

Catalytic region

At above 100 torr aldehyde concentrations, only catalysis exists at any NO concentration. In this region, the rate of decomposition was found to be proportional to $p_{NO}^{1/2}$. If the 3/2 order rate constants k' (presented in Table II) are divided by the square root of p_{NO} , then the rate constant values tend to be independent of the NO and aldehyde concentrations (within the limits of experimental error), as it can be seen in Table III.

Using the mean values of these rate constants (Table IV), the overall activation energy of the NO influenced decomposition was determined from the temperature

Table III

 $k'/p_{\text{NO}}^{1/2} \cdot 10^{-2}$ values at 512 °C at different NO and aldehyde pressures

P_{NO} (torr) \ P_{ald} (torr)	10	20	35	50
25	1.0226	0.9820	1.0531	1.0948
50	1.0318	0.9872	0.9857	0.9104
100	1.0573	1.0724	1.0447	1.0875
200	1.2247	—	1.0709	1.0587

dependence of $k'/p_{\text{NO}}^{1/2}$ for the catalytic region. These values are:

$$E_a = 41.38 \pm 0.79 \text{ kcal/mole.}$$

$$A = 3.618 \pm 0.214 \cdot 10^{12}$$

(at 25—200 torr aldehyde and 10—50 torr NO concentrations). The Arrhenius parameters obtained in this way are comparable with LAIDLER and EUSUF's values,

$$k = 2.2 \cdot 10^{12} \exp -43.5/RT \text{ l}^{1/2} \text{ mole}^{-1} \text{ sec}^{-1}$$

(at 100 torr aldehyde and 50 torr NO concentration).

Inhibition region

On the basis of our experimental data, only qualitative remarks can be given for this region of reactions. The appearance of inhibition is the function of aldehyde and NO concentration. Above 100 torr initial aldehyde concentration, inhibition is practically impossible to be detected, since a small amount of NO (~ 0.5 torr) causes a significant catalysis. The inhibition region caused by NO is very narrow (it is observable up to max. 5—6 torr NO) and the inhibition is inversely proportional to the aldehyde concentration. The inhibition region significantly increases with the temperature (for example at 50 torr initial aldehyde concentration, 50 °C temperature rise increased the inhibition region to the threefold). The degree of inhibition also increases, as can be seen from Fig. 8.

Fig. 8 shows that the value of the rate minimum (the maximally inhibited rate) shifts towards lower NO concentrations, due to the effect of temperature rise. This behaviour is in contradiction with that found by MÁRTA and SZABÓ [15] in the propionaldehyde—NO system, where the value of the rate minimum shifts towards higher NO concentrations. This fact is interpreted by the authors considering that, at higher temperatures, the primary steps take place much more often, thus the radical concentration is higher and to remove this higher radical concentration more NO is needed. A similar effect of temperature on the degree of inhibition was found in the investigation of RICE and VARNERIN [6]. In contrary to our observations, EUSUF and LAIDLER [8] found the degree of inhibition to decrease with temperature.

Table IV

Mean values of $k'/p_{\text{NO}}^{1/2} = \bar{k}$ at different temperatures ($k' \cdot 10^{-2}$ values in $\text{l}^{1/2} \text{ mole}^{-1} \text{ sec}^{-1}$, p_{NO} in torr)

t °C	\bar{k}
512	1.0456 ^a
527.5	1.8073 ^a
539.5	2.5980 ^b
550.5	3.6578 ^c

Notes

- (a) Average of 15 data
- (b) Average of 12 data
- (c) Average of 7 data

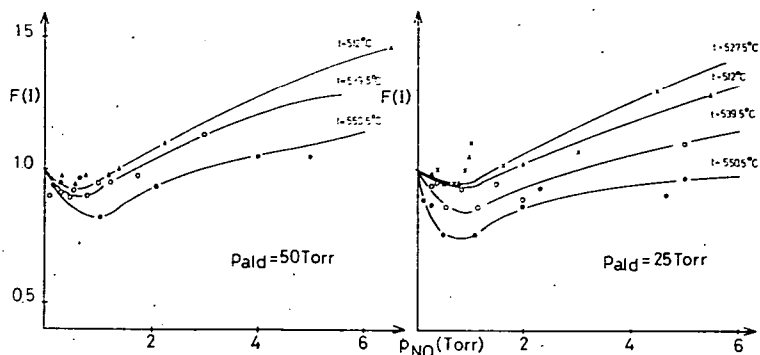


Fig. 8. Temperature dependence of influencing curves in the inhibited region. $p_{ald} = 50$ torr and 25 torr. $t = \times 527.5^\circ\text{C}$; $\Delta 512^\circ\text{C}$; $\circ 539.5^\circ\text{C}$; $\bullet 550.5^\circ\text{C}$ at 25 torr aldehyde. $t = \Delta 512^\circ\text{C}$; $\circ 539.5^\circ\text{C}$; $\bullet 550.5^\circ\text{C}$ at 50 torr aldehyde

As well known, oxygen in very small amounts ($\sim 10^{-3}\%$) exerts a strong catalytic effect on the decomposition of aldehyde [14], and changes very significantly the rate of NO influenced decomposition. In the presence of trace amounts of oxygen, we observed significant inhibition at 200 torr initial aldehyde concentration, at which concentration under oxygen-free conditions, only catalysis could be observed.

Analytical survey of products

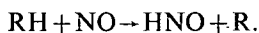
In some cases our experiments were connected with GC analysis. These measurements were made at 512°C with two aldehyde concentrations (80 and 50 torr) and four NO concentrations (0.75, 10, 20, 40 torr), which cover both the catalytic and inhibition regions.

The effect of NO on major products

Some typical concentration—time plots for CH_4 and CO formation in the presence of NO are shown in Figs. 9 and 10, respectively, where the results of experiments at 512°C , at 80 torr aldehyde pressure and at different NO concentration are plotted. This reaction mixture represents the catalytic region.

It can be seen from the Figs 9 and 10 that the shapes of the curves representing the formation of major products in the presence of NO do not change, however strongly the amount of major products increases with the increase in NO concentration. This increase is observable in the pressure—time curves, too (Fig. 2). In the maximally inhibited region, as it can be seen in Fig. 11, this increase is smaller but definitely exists.

This increase in the concentration of major products with increasing NO concentration can be interpreted by supposing that the NO reacts with the aldehyde molecule, abstracting hydrogen and producing R radicals, which can continue the chain



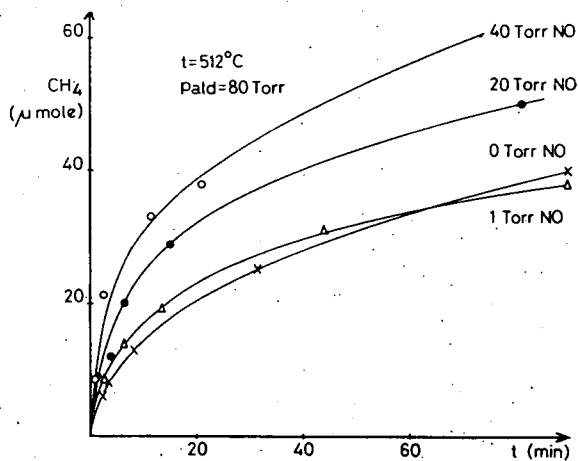


Fig. 9. Formation of CH_4 as function of time at different NO concentrations (catalytic region) $t = 512^\circ\text{C}$, $p_{\text{ald}} = 80$ torr; p_{NO} : Δ 0 torr; \times 1 torr; \bullet 20 torr; \circ 40 torr

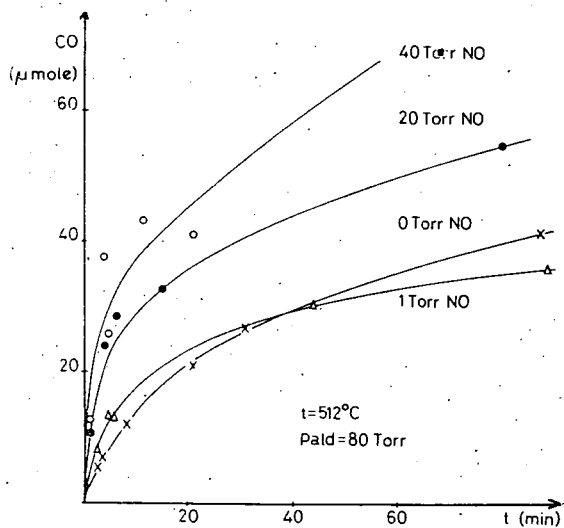


Fig. 10. Formation of CO as function of time at different NO concentrations (catalytic region) $t = 512^\circ\text{C}$, $p_{\text{ald}} = 80$ torr; p_{NO} : \times 0 torr; Δ 1 torr; \bullet 20 torr; \circ 40 torr

From the Figs 9 and 10 it can also be seen that in absence of NO, the amounts of CH_4 and CO agree well, while in the presence of NO, the amount of CO exceeds that of CH_4 , especially at higher conversions. This experimental fact has not been observed by other authors. It is to be explained by assuming that a greater part

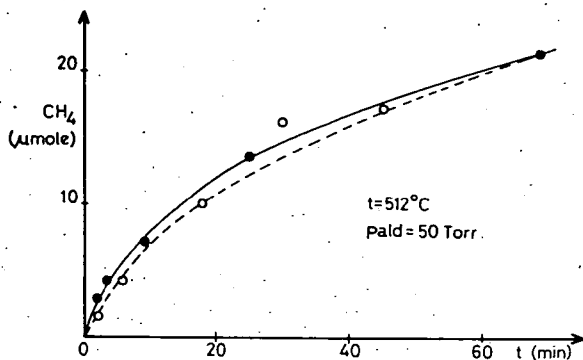


Fig. 11. Formation of CH_4 as function of time at 512°C (inhibited region) $p_{\text{ald}} = 50$ torr: p_{NO} : \circ 0 torr; \bullet 0.75 torr

of methyl radicals, mainly at higher NO concentrations, are in the form of RNO and not in the form of free methyl radicals. The former does not produce CH_4 at all in the reaction.

From the initial rate values, calculated from the curves of the formation of major products, the partial order related to NO was found to be 0.61, in agreement with the value calculated from pressure—time measurements.

In the maximally inhibited region (50 torr acetaldehyde + 0.75 torr NO) there is no difference in the amount of major products within limits of experimental error.

The effect of NO on minor products

H_2 . Among the minor products, hydrogen forms in the greatest amount. A typical H_2 yield—time curve is given in Fig. 12, showing the analysis data of a series of experiments carried out at 512°C , at 80 torr aldehyde pressure and at different pressures of NO.

The shape of these curves does not change in the presence of NO, and remains similar to the curves of major products due to the effect of NO; however, the hydrogen yield increases markedly. The degree of this increase is higher than in the case of major products. As it can be seen, e.g. from Fig. 12, after an hour pyrolysis time, the increase of the amount of major products is twofold, while in the case of hydrogen is 6fold. This increase in hydrogen formation takes place in the maximally inhibited region too, but in a smaller extent (Fig. 13). This fact indicates that in both regions the formation of hydrogen takes place with the same mechanism.

Acetone, ethane, ethylene. In the presence of NO, the amount of acetone formed does not change significantly, while that of ethane and ethylene slightly

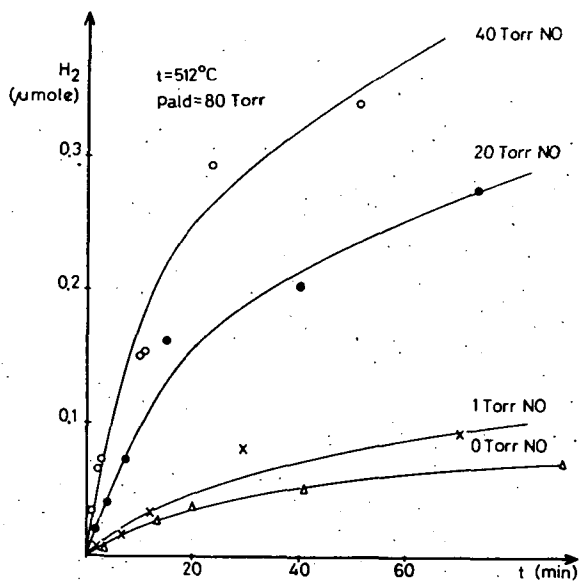


Fig. 12. Formation of H_2 as function of time at different NO concentrations (catalytic region) $t = 512^\circ\text{C}$, $p_{\text{ald}} = 80$ torr; p_{NO} Δ 0 torr; \times 1 torr; \bullet 20 torr; \circ 40 torr.

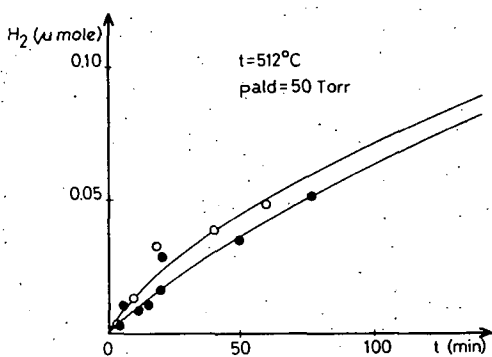


Fig. 13. Formation of H_2 as function of time at 512°C . (inhibited region) $p_{\text{ald}} = 50$ torr; p_{NO} : \bullet 0 torr; \circ 0.75 torr.

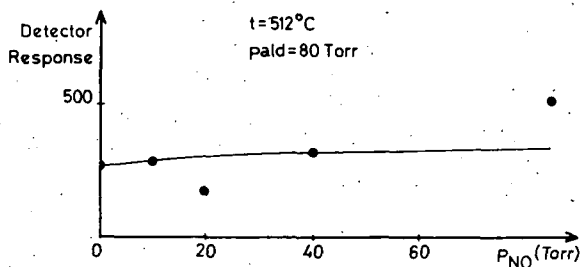


Fig. 14. Formation of acetone as function of NO concentrations at 512°C , $p_{\text{ald}} = 80$ torr. (The amount of acetone was measured at 50% conversion)

increases, as seen from Figs 14–16. These observations are in agreement with literature [9].

HCN. It is a general observation that in the pyrolysis of organic compounds in the presence of NO, HCN is always an easily detectable product. A typical HCN formation curve is shown in Fig. 17. It can be clearly seen that the formation of HCN takes place with an induction period, which indicates that HCN is a secondary

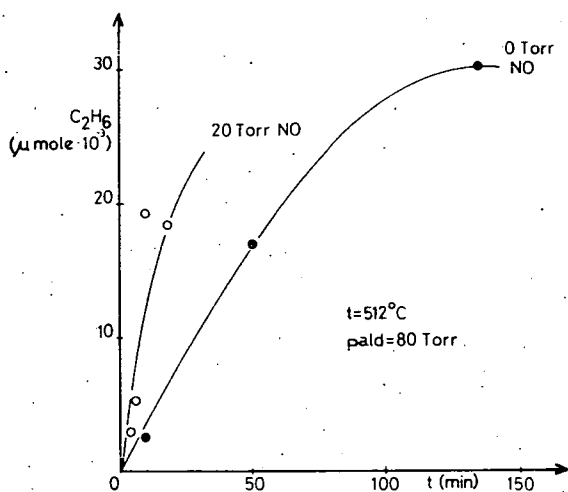


Fig. 15. Formation of ethane as function of time at 512°C (catalytic region) $p_{ald}=80 \text{ torr}$; p_{NO} : ● 0 torr; ○ 20 torr

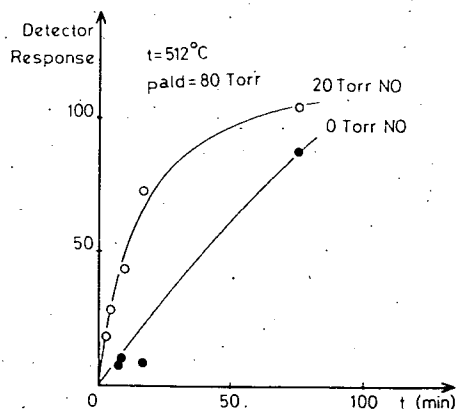


Fig. 16. Formation of ethylene as function of time at 512°C . (catalytic region) $p_{ald}=80 \text{ torr}$; p_{NO} : ● 0 torr; ○ 20 torr

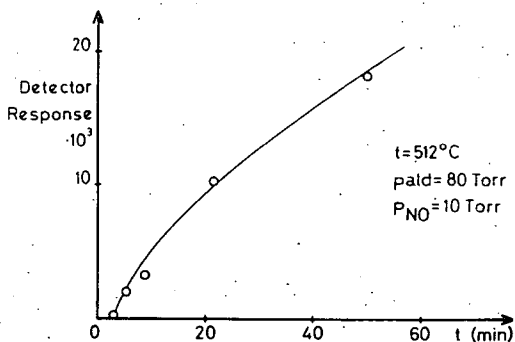


Fig. 17. Formation of HCN as function of time at 512°C (catalytic region) $p_{ald}=80 \text{ torr}$, $p_{NO}=10 \text{ torr}$

product. The shape of HCN formation curves is similar to that of major products, and the amount of HCN formed increases proportionally to NO concentration, as seen from Fig. 18, where the amount of HCN, obtained in the pyrolysis of 80 torr aldehyde at 50% conversion, is plotted against NO concentration.

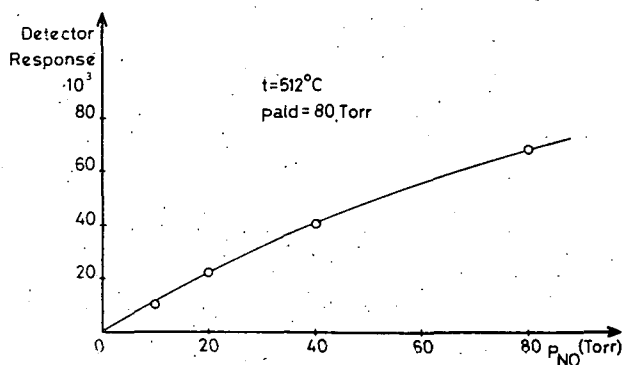


Fig. 18. Formation of HCN as function of p_{NO} at 512°C $p_{\text{alid}} = 80 \text{ torr}$

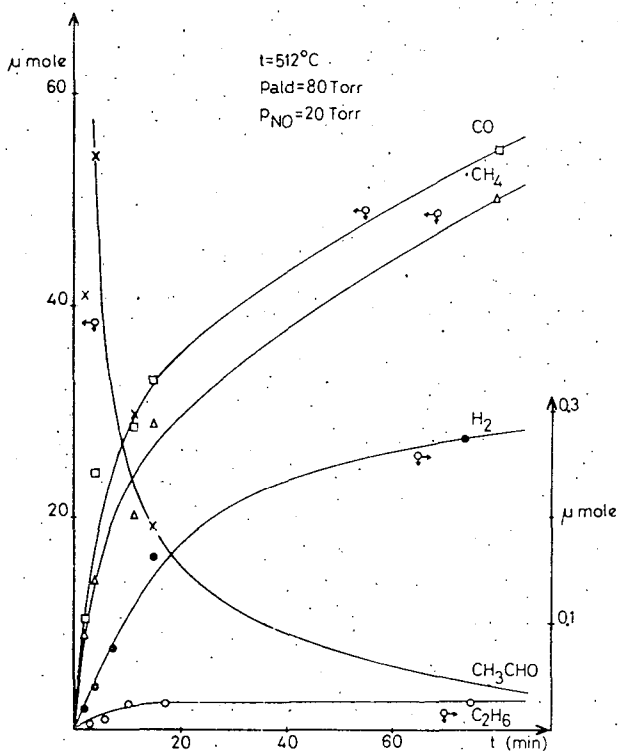


Fig. 19. Mass-balance curves at 512°C (catalytic region) $p_{\text{alid}} = 80 \text{ torr}$. $p_{\text{NO}} = 20 \text{ torr}$. \square CO; Δ CH₄; \bullet H₂; \times CH₃CHO; \circ C₂H₆.

It is to be noted that, besides the products mentioned above, N_2 , N_2O , H_2O , CO_2 could also be detected with the MS technique. A typical mass balance curve of the pyrolysis products at 512 °C of 80 torr aldehyde and 20 torr NO (catalysis region) is to be seen in Fig. 19.

Discussion

It can be seen from our experimental results that, in the presence of NO, in the catalytic region the amounts of major and minor products increase. This is in agreement with the findings of other authors [7, 9]. The increase in concentration of major products can be interpreted by the chain initiation role of NO. So besides the initiation process,



we have to take into consideration the step



too. This step was first suggested by WOJCIECHOWSKI and LAIDLER [16] as an initiation step in NO influenced pyrolyses of organic compounds. These steps are followed by the decompositions



which, at the temperature of pyrolysis (500 °C), take place instantly.

The further reactions of methyl radicals are the following:



The ratio of these two rate constants (k_6/k_7), on the basis of literature, is about 10 [22, 23].

Part of the methyl radicals reacts with NO in an equilibrium reaction, forming nitrosomethane [17, 18]



The nitrosomethane, formed in step (8) could isomerize to formaldoxime [26]

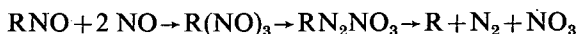


which later decomposes



into water and HCN. In the direct decomposition of formaldoxime, TAYLOR and BENDER [27] has found, among others, NH_3 and CO as products, but these results were confirmed neither by other authors nor by our results. The steps (8), (9) and (10) show one route of NO consumption. Another route (*i.e.* further reactions

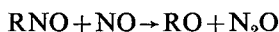
of nitrosomethane) was first described by BROWN [19]. According to BROWN the nitrosomethane reacts with NO at higher NO concentrations



and gives N_2 and R radical, while the NO_3 in the $\text{NO}_3 + \text{NO} \rightarrow 2 \text{NO}_2$ reaction gives a stable product.

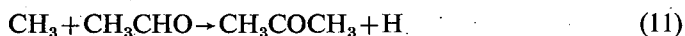
On the basis of our experimental data, the existence of this type of NO consumption is confirmed. Similar reactions were established by CHRISTIE and EDWARDS [20] in the photolysis of acetaldehyde—NO system, and by EASTMOND and PRATT [28] in the pyrolysis of ethane and butane in the presence of NO.

The reaction



supposed by CHRISTIE [21] has to be rejected, because we could not detect any products originating from further reactions of methoxy radicals. N_2O , which was detected in our system, probably formed in another way (maybe in the "cold reaction" mentioned by SCHUCHMANN and LAIDLER).

According to our analytical results, the amount of acetone does not change significantly in the presence of NO, so the consideration of a new acetone forming reaction, besides the



step, is not necessary.

The great increase in the hydrogen formation in the presence of NO can be explained, besides the steps



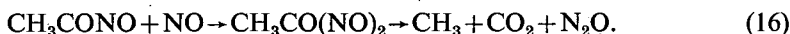
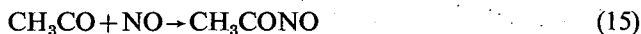
with (11), (4), and (5) as a new step.

The slight increase in formation of ethylene in the presence of NO can be interpreted on the basis of LAIDLER's mechanism, because, according to step



with the increase of H atom concentration the rate of ethylene formation also increases.

The formation of CO_2 and N_2O , detected by MS method, can be described with the following reactions:



Step (15), which was supposed by several authors at room temperature photolyses [24, 29, 30] is only to be regarded as formal because its existence at higher temperatures is questionable.

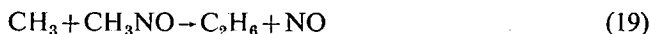
Besides the termination steps described for the decomposition in the absence of NO



and

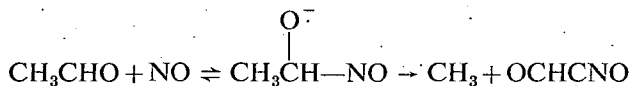


the following new termination steps take place:



The CO formed in step (20) could give a contribution to the experimentally found CO overproduction.

During our investigations, we were not able to detect CH_3NCO . So the existence of a new NO addition step, described by SCHUCHMANN and LAIDLER [9]



was not confirmed by us. According to this step, numerous products containing CN (so CH_3NCO , too) should form.

The elementary steps summarized above are suitable for interpreting the main features of the influenced reaction both in the inhibited and catalytic regions.

This elementary steps account also for the change in the distribution of products found experimentally.

* * *

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ИЗУЧЕНИЕ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ АЦЕТАЛЬДЕГИДА В ПРИСУТСТВИИ ОКИСИ АЗОТА

И. Барди, Ф. Марта

Изучен пиролиз ацетальдегида при температурах 496—550 °С, при давлениях ацетальдегида 25—200 торр и окиси азота 0—50 торр. За кинетикой разложения следили по давлению смеси и газохроматографическим методом. Разными методами определены порядки реакции разложения относительно ацетальдегида и окиси азота. На основании данных по измеренным давлениям выведены „кривые влияния”, на основании которых пришли к определенным выводам относительно областей индукции и катализа. В каталитической области были определены Аррениусовые параметры для общей реакции. Изучено влияние окиси азота на образование основного продукта и некоторых других продуктов разложения (H_2 , C_2H_4 , C_2H_6 , HCN , и CH_3COCH_3) как в каталитической, так и ингибиционной областях реакции. Кратко рассмотрены механизмы образования продуктов и предлагается простой механизм разложения ацетальдегида в присутствии окиси азота.