

Kinetic Studies and Mechanism of the Reaction of Propylene with Nitric Oxide for Acrylonitrile Synthesis in the Presence of Nickel Oxide on Alumina Catalysts

F. ZIDAN,¹ G. PAJONK, J. E. GERMAIN, AND S. J. TEICHNER

Université Claude Bernard (Lyon I), L. A. au CNRS No. 231 de Catalyse Appliquée et Cinétique Hétérogène, 43 Boulevard du 11 Novembre 1918, 69621-Villeurbanne, France

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The reaction of propylene with nitric oxide for the synthesis of acrylonitrile has been studied over nickel oxide supported on alumina as catalyst. A xerogel catalyst of composition 2NiO , Al_2O_3 was prepared by thermal decomposition, under vacuum at 400°C , of a nickel hydroaluminate, 2NiO , Al_2O_3 , $8\text{H}_2\text{O}$. Aerogel catalysts $\text{NiO}-\text{Al}_2\text{O}_3$ and $\text{NiO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ of variable compositions were prepared by the autoclave method (hypercritical conditions). All these solids are selective (80%) in the formation of acrylonitrile at 410°C . The best catalytic activity and selectivity are observed after a previous activation of the catalyst by oxygen at 410°C for 48 hr. The kinetic studies reveal that the mechanism of the reaction is of the "redox" type. First there is reduction of the catalyst by propylene with formation of dehydrogenated radicals; these then form acrylonitrile with atomic nitrogen released by the dissociation of nitric oxide which reoxidizes the catalyst. The behavior of xerogel catalyst ($\text{Ni}/\text{Al} = 1$) and of aerogel catalysts (Ni/Al varying between 0.2 and 1) is similar for the same composition. The formation of acetonitrile is attributed to the oxidation of acrylonitrile over a fresh catalyst (barley reduced). The formation of carbon dioxide devolves from the oxidation of acrolein.

INTRODUCTION

The catalytic ammoxidation of propylene into acrylonitrile by an ammonia-oxygen mixture has been widely studied, mostly over Bi-Mo-O- or Sb-Sn-O-type catalysts (1-4). The ammonia excess which produces polymerization of the acrylonitrile and other secondary reactions is frequently eliminated as ammonium sulfate (1). Employing nitric oxide instead of the NH_3-O_2 mixture suppresses this disadvantage and also facilitates the thermal control of the reaction. Indeed, the synthesis of the acrylonitrile through the reaction between

propylene and nitric oxide was attempted on lead oxide supported on TiO_2 , SnO_2 , or ZrO_2 , catalysts (5-7) and on a catalyst based on silver deposited on silica (8).

Although many studies concerning the mechanism of the formation of acrylonitrile by ammoxidation have been published, the mechanism of the reaction between propylene and nitric oxide has never been described. One possible route in the ammoxidation of propylene to acrylonitrile involves the partial oxidation of ammonia to oxides of nitrogen followed by their reaction with propylene or with acrolein formed in the first step (9). But in general, in the $\text{NH}_3 + \text{O}_2$ process a direct route is assumed (no NO intermediate) either (1)

¹ Present address: Université el Azher, Faculté des Sciences, Département de Chimie, Le Caire, Egypte.

by interaction between dehydrogenated surface radicals C_3H_y ($y < 6$) and NH_x ($x < 3$), giving either directly the acrylonitrile or an imine which is oxidized to acrylonitrile (2, 3) or (ii) by oxidation to acrolein which is then converted into acrylonitrile by ammonia and oxygen (10, 11). The system Mo-Bi-O was used in many of these investigations, and although the proposed reaction models differ in details (12-15) possibly as a result of the differences in the experimental conditions, they all agree that the ammoxidation of propylene is a "redox" type reaction, as suggested earlier for the partial oxidation of olefins (16).

In the present study, a new type of catalyst based on nickel oxide supported on alumina is investigated in the formation of acrylonitrile by interaction between propylene and nitric oxide (17). This catalytic system was previously found to be selective in the partial oxidation of isobutene and isobutane (18, 19). The best selectivity to acrylonitrile (80%) was obtained with a catalyst pretreated in oxygen at 410°C and for propylene-rich mixtures ($C_3H_6/NO = 9/1$). The mechanism proposed here is also based on the "redox" model in which the catalyst is reduced by propylene and reoxidized by nitric oxide dissociated into oxygen and atomic nitrogen.

EXPERIMENTAL

1. Preparation of the Catalyst

(a) *Xerogel 2NiO, Al₂O₃*. This catalyst was prepared by the thermal decomposition at 400°C under vacuum of the nickel hydroaluminate, $2NiO, Al_2O_3, 8H_2O$ (18, 20). Its surface area is 246 m²/g and its pore volume is 0.28 cm³/g. X-ray diffraction shows that alumina is amorphous while nickel oxide is crystallized. The ratio Ni/Al of this catalyst is equal to 1.

(b) *Aerogel catalysts NiO-Al₂O₃*. In order to vary the ratio Ni/Al and to conserve

the amorphous character of the alumina carrier, aerogel catalysts were prepared. A solution of aluminum *s*-butylate in *s*-butanol and a solution of nickel acetate in methanol were mixed in corresponding proportions and hydrolyzed by the stoichiometric amount of water (21, 22). The solvents were evacuated under hypercritical conditions in an autoclave. Five catalysts were prepared with different Ni/Al ratios (from 0.2 to 1). Their surface areas are given in Table 2. As for xerogel, X-ray data show that alumina is amorphous and nickel oxide is crystallized (22).

(c) *Aerogel catalyst NiO-Al₂O₃-SiO₂*. This was also prepared by the autoclave method after addition of silicon methylate (in methanol) to the previous solution. The Ni/(Al + Si) ratio for this catalyst is equal to 2/5, and the proportion of alumina is 10%. Its surface area is 620 m²/g.

2. Catalytic Reactor and Procedure

The reaction was carried out in a differential dynamic microreactor with a low conversion (<10%) in order to avoid mass transfer effects. The amount of catalyst was of the order of 0.2 to 0.3 g. The volume composition of reagents was set in the ratio $NO:C_3H_6:He = 1:9:5$. The total flow rate at atmospheric pressure of 1.8 liters/hr determines a contact time between 0.18 and 0.27 sec. It was found that the catalyst activated before the reaction by an oxygen flow at 410°C for 48 hr was more active and more selective toward the formation of acrylonitrile (17) and was stable over a period of many hours. The tests were carried out at 410°C, and the main products of the reaction were acrylonitrile, acetonitrile, and carbon dioxide. However, before the steady state was achieved small amounts of acrolein, acetone, acetaldehyde, and ethylene were also detected. Also traces of ammonia were identified during all runs. After the run, chemical analysis of catalysts always

TABLE 1
The Influence of the Composition of the Feed on the Rates of Formation
and the Selectivities of Various Products

Feed composition (NO:C ₃ H ₆ :He)	$R_{C_3H_3N}$ (10 ⁻⁸ mol/sec/g)	$R_{C_2H_3N}$ (10 ⁻⁸ mol/sec/g)	R_{CO_2} (10 ⁻⁸ mol/sec/g)	$S_{C_3H_3N}$ (%)	$S_{C_2H_3N}$ (%)	S_{CO_2} (%)
1:0.66:0	8	1	20	15	3	82
1:2:4.5	122	8	50	65	6	29
1:9:5	190	10	36	79	7	14

showed the presence of metallic nickel and carbon. The results are represented as the rate (R) of propylene consumption or of products formation as a function of the partial pressures of propylene and nitric oxide. The analysis of effluents was made by gas chromatography.

RESULTS AND DISCUSSION

1. Activity and Selectivity of Various Catalysts

(a) *Influence of the composition of the feed and of the reaction conditions.* The stoichiometric equation for the formation of acrylonitrile,

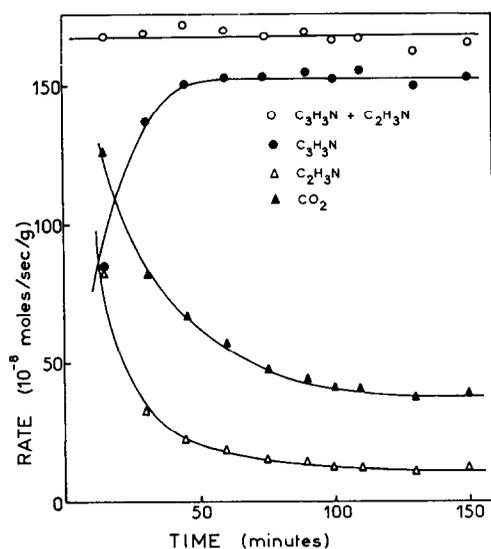
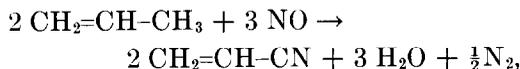
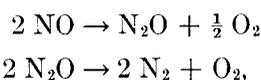


FIG. 1. Rates of formation of various reaction products at 410°C vs time-on-stream.

implies a ratio NO/C₃H₆ equal to 1.5. But NO is also a source of oxygen resulting from its disproportionation over the catalyst,



and a NO deficient mixture (NO:C₃H₆:He = 1:9:5) is preferred (5). The catalytic activities [or rates of formation (R)] and the selectivities (S) of various reaction products at the steady state depend on the proportion of nitric oxide, as is shown in Table 1.

The activity and the selectivity toward the nitriles (C₃H₃N and C₂H₃N) increase markedly by decreasing the proportion of nitric oxide below the stoichiometric ratio (first line of Table 1). Simultaneously, the

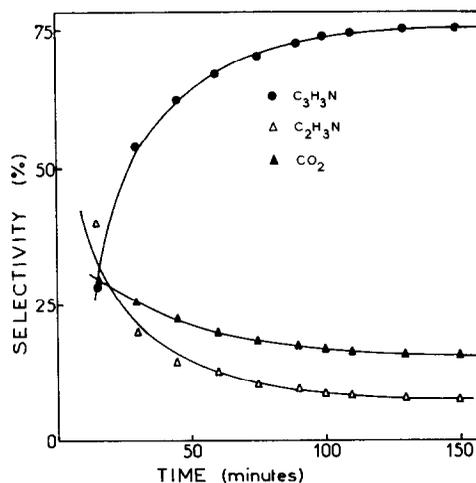


FIG. 2. Selectivities toward various products at 410°C vs time-on-stream.

TABLE 2
The Selectivities of Aerogel Catalysts

Aerogel (NiO-Al ₂ O ₃) Ni/Al	Surface area (m ² /g)	$\frac{R_{C_3H_3N}}{R_{C_2H_3N}}$	Selectivity (%)				
			C ₃ H ₃ N	C ₂ H ₃ N	CO ₂	C ₂ H ₄	C ₃ H ₆ O
0.2	533	6.5	70	16	9	2.5	2.5
0.4	514	7.8	72.5	14.5	11	1.0	1.0
0.6	403	9.8	75	11.5	10.5	1.3	1.7
0.8	—	11.8	78	9	10.5	0.8	1.5
1.0	—	13.0	77	9	11	0.8	1.6

selectivity toward total oxidation, given by S_{CO_2} , decreases.

Figures 1 and 2 show the evolution of the initial catalytic activity (R) and selectivity (S) for the main reaction products toward those of the steady state. The activity and the selectivity in the formation of acrylonitrile sharply increase during the transition period, whereas those of acetonitrile and CO₂ decline. Figure 1 also gives the sum of rates of formation of both nitriles which remains constant over the run. This result tends to show that acetonitrile results from the oxidation of acrylonitrile on a fresh catalyst (not yet reduced and not yet covered with carbon). Similar results were reported (14) for the oxidation of acrylonitrile into acetonitrile over a MoO₂ catalyst which decreases when the catalyst becomes reduced and covered by carbon. At the steady state (Fig. 2) the selectivities to acrylonitrile (79%) and acetonitrile (7%) indicate that the "used" catalyst is now almost inactive for the decomposition of acrylonitrile.

(b) *Influence of the ratio Ni/Al.* The reaction trend, as depicted by Figs. 1 and 2, for the xerogel catalyst remains very similar for aerogel catalysts with the ratio Ni/Al varying from 0.2 to 1. In particular, almost the same activities and selectivities for various reaction products are observed for the xerogel catalyst (Ni/Al = 1) and for the aerogel catalyst having the same Ni/Al ratio. Table 2 shows at the steady state for these catalysts of various composition the selectivities for reaction products and the ratio of the rates of formation of the two nitriles for the feed composition NO:C₃H₆:He = 1:9:5.

The selectivity toward the formation of nitriles (C₃H₃N and C₂H₃N) is high for all aerogel catalysts, but when the ratio Ni/Al increases, the selectivity to acrylonitrile increases, the selectivity toward the total oxidation (S_{CO_2}) remaining almost independent of this ratio.

Finally, pure nickel oxide xerogel, prepared by the decomposition of nickel hydroxide shows a very poor stability with

TABLE 3
Properties of NiO-Al₂O₃-SiO₂ Aerogel Catalyst

Time (min)	Selectivity (%)				
	Acrylonitrile	Acetonitrile	Acetone	Acrolein	Ethylene
10	63	14	16	4	3.0
60 (steady state)	76	9	7.5	4	3.2

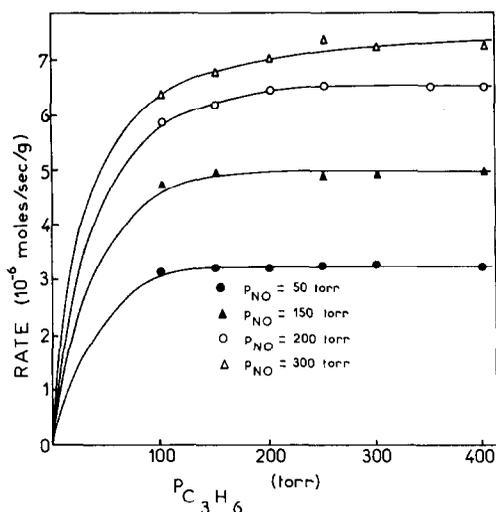


FIG. 3. The influence of the partial pressure of propylene on the rate of its consumption by reaction with NO at 410°C.

time-on-stream, though the initial formation of acrylonitrile is of the same order of magnitude as for supported nickel oxide catalysts.

The ternary aerogel NiO–Al–SiO₂, which is more acidic than binary aerogels (18), can be used to test a possible influence of the acidity on the orientation of the reaction with propylene, performed here in the absence of NH₃. Table 3 shows the selectivities into various reaction products (feed composition NO:C₃H₆:He = 1:9:5), and it should be noticed that more than traces of acetone, acrolein, and ethylene are obtained here. This is opposite to the behavior of binary catalysts. Moreover, the rate of formation of CO₂ corresponds to the rate of formation of C₂ products, and therefore there is no production of CO₂ from the total oxidation reaction ($S_{CO_2} = 0$). However, the rate of formation of acrylonitrile is smaller than the rate registered with binary catalysts by a factor of 4. Finally, Table 3 also shows that the steady state (constant activity and selectivity) is achieved faster than for binary catalysts (Fig. 2). Also, during the first period of the reaction (10 min in Table 3), the

formation of acetonitrile from acrylonitrile is very much reduced as compared to that on the binary catalysts (Fig. 2). It is inferred from these results that the acidic character of ternary aerogel catalyst favors the deposit of carbon and the reduction of NiO at the very beginning of the reaction, and this property (i) suppresses the aptitude for the total oxidation of propylene, (ii) decreases very rapidly the amount of acrylonitrile oxidized into acetonitrile, and (iii) allows a faster achievement of the steady state.

II. Kinetic Studies and Reaction Mechanism

(a) *Influence of partial pressures of reagents.* In the first series of experiments the partial pressure of propylene was varied by dilution with helium while the partial pressure of NO was maintained constant (total pressure = 760 Torr). In the second series of experiments these conditions were reversed. In both cases the mixture NO–C₃H₆–He was passed over 0.2 g of xerogel catalyst at 410°C with a total flow rate of 1.8 liters/hr (contact time, 0.18 sec). The rates were recorded at the steady state for each mixture.

Figures 3 and 4 show the influence of the partial pressure of propylene on the rate of propylene consumption (Fig. 3) and on the rate of formation of acryloni-

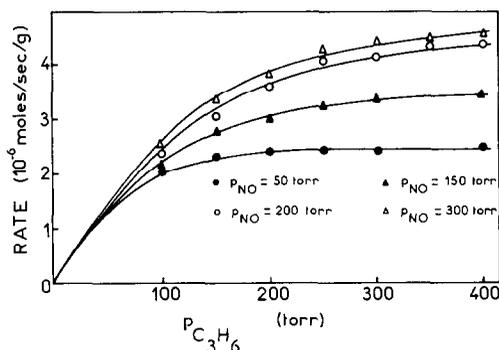
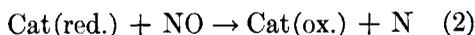
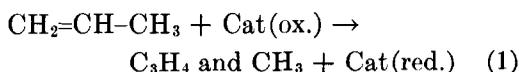


FIG. 4. The influence of the partial pressure of propylene on the rate of formation of acrylonitrile at 410°C.

trile (Fig. 4). An identical set of data represents the influence of the partial pressure of nitric oxide (Figs. 5 and 6). In addition, it was observed that the rate of formation of acetonitrile was constant, irrespective of the partial pressures of propylene and of nitric oxide (partial orders, 0).

The kinetics and mechanism of the conventional ammoxidation ($\text{NH}_3 + \text{O}_2$) of propylene have been studied extensively. The formation of allylic radicals was established by isotope techniques (23, 24) and led to the generally accepted view that the first step in the catalytic oxidation or ammoxidation of olefins is the abstraction of hydrogen atom(s) from the olefin and the reduction of the oxide catalyst which is then reoxidized by oxygen ("redox" mechanism) (16).

The same type of mechanism emerges from this study. It involves the reduction of the catalyst by propylene, leading to the formation of radicals of C_3H_4 and C_3H_3 type and then the reoxidation of the catalyst by nitric oxide which is decomposed into atomic nitrogen:



The atomic nitrogen reacts (fast step) with a C_3H_3 radical to form acrylonitrile:



Applying the "redox" mechanism (16) the rate of step (1) is given by:

$$R_r = k_r p_{\text{C}_3\text{H}_6} \theta_{\text{NO}}, \quad (3)$$

where R_r is the rate of reduction of the oxidized catalyst, k_r the rate constant, and θ_{NO} the coverage by NO which determines the state of oxidation of the catalyst.

The rate of step (2) is given by:

$$R_o = k_o p_{\text{NO}} (1 - \theta_{\text{NO}}),$$

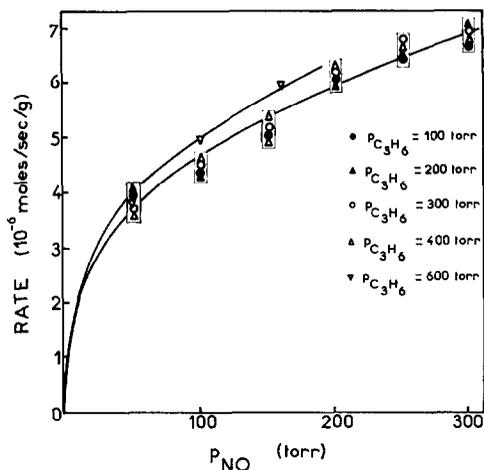


FIG. 5. The influence of the partial pressure of nitric oxide on the rate of propylene consumption at 410°C .

where R_o is the rate of reoxidation of the reduced catalyst, k_o the rate constant, and $(1 - \theta_{\text{NO}})$ the surface uncovered by NO which determines the state of reduction of the catalyst. At steady-state conditions, neglecting the rate of desorption of NO,

$$k_o p_{\text{NO}} (1 - \theta_{\text{NO}}) = k_r p_{\text{C}_3\text{H}_6} \theta_{\text{NO}}.$$

Then

$$\theta_{\text{NO}} = \frac{k_o p_{\text{NO}}}{k_o p_{\text{NO}} + k_r p_{\text{C}_3\text{H}_6}}. \quad (4)$$

The rate of the reaction between propylene and NO is given by Eq. (3) which becomes, by substitution of Eq. (4):

$$R_r = \frac{k_r k_o p_{\text{NO}} p_{\text{C}_3\text{H}_6}}{k_o p_{\text{NO}} + k_r p_{\text{C}_3\text{H}_6}}, \quad (5)$$

or in the linear form:

$$\frac{1}{R_r} = \frac{1}{k_o p_{\text{NO}}} + \frac{1}{k_r p_{\text{C}_3\text{H}_6}}. \quad (6)$$

For p_{NO} constant and $p_{\text{C}_3\text{H}_6}$ variable and also for these conditions reversed, the plots $1/R_r = f(p_{\text{C}_3\text{H}_6})^{-1}$ and $1/R_r = f(p_{\text{NO}})^{-1}$ should be parallel straight lines.

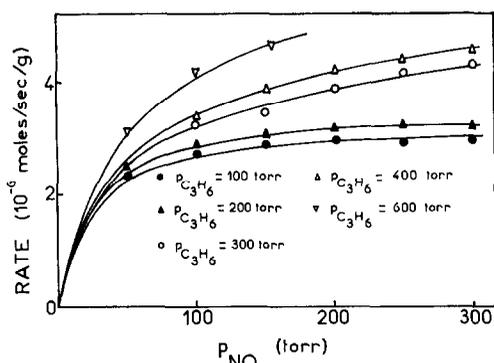


FIG. 6. The influence of the partial pressure of nitric oxide on the rate of formation of acrylonitrile at 410°C.

The results of Figs. 3 and 5 plotted according to this representation (Figs. 7 and 8) show that this is the case for the rate of propylene consumption. Similarly, the rate of formation of acrylonitrile (Figs. 4 and 6) follows the same plots (Figs. 9 and 10) with a small variation of slopes of the straight lines (at the most for one or two lines).

Table 4 gives the mean values of k_r and k_o calculated from Figs. 7 to 10.

The computed values for k_r and k_o for both reactions (A) and (B) are within the same order of magnitude and give therefore a consistent support to the "redox" mechanism of the interaction between propylene, nitric oxide, and the catalyst.

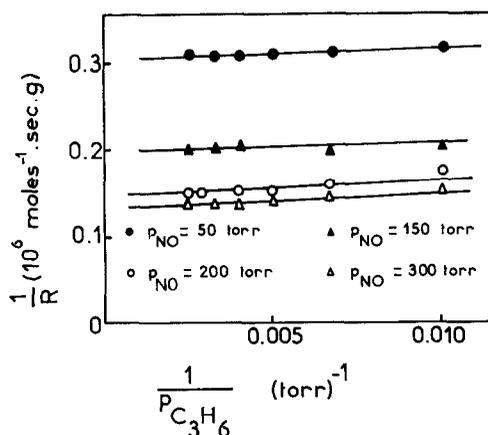


FIG. 7. Linear conversion (see text) of Fig. 3.

The nature of the intermediate steps leading to acrylonitrile from dehydrogenated radicals (C₃H₄ and C₃H₃) and atomic nitrogen, left by NO after reoxidation of the catalyst, should be also described. Now, the hypothesis of the formation of atomic nitrogen was formulated even in the case of ammoxidation of propylene by the conventional mixture (NH₃ + O₂) (1, 25). The formation of N from NO may be already suspected from the detection of traces of ammonia during the reaction, provided the catalyst is inactive in the synthesis of NH₃ from dinitrogen, always present because of a partial dismutation of NO and of a decomposition of generated N₂O. Indeed, an

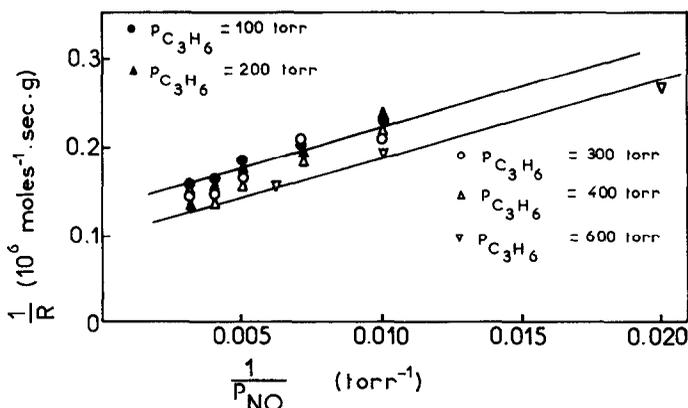
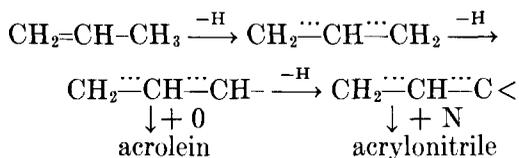


FIG. 8. Linear conversion (see text) of Fig. 5.

attempt at the synthesis of ammonia from the elements on the xerogel catalyst at 410°C completely failed, whereas a quantitative formation of ammonia was observed from the mixture H₂-NO. The catalyst is therefore unable to dissociate N₂ to form ammonia but it dissociates NO, probably because oxygen of NO is required to oxidize the reduced catalyst (26).

(b) *Mechanism of reactions.* The mechanism of formation of acrolein or of acrylonitrile in the partial oxidation or in the ammoxidation of propylene assumes that this molecule gradually loses hydrogen (13, 23, 24):



Two possibilities exist for dehydrogenated radicals: (i) The radical C₃H₁ may react

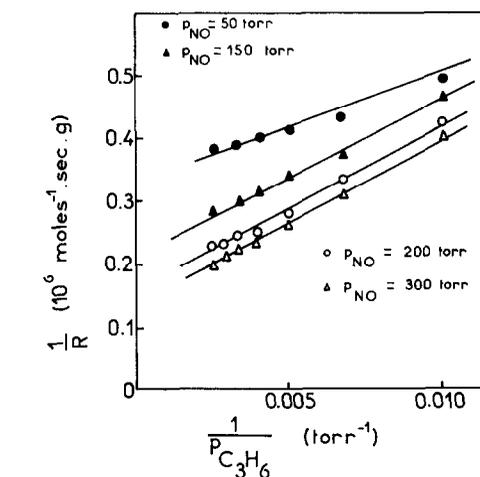


FIG. 9. Linear conversion (see text) of Fig. 4.

with the radical NH (formed by extraction of H by atomic N) to form first an imine which is then oxidized to acrylonitrile (13), or (ii) the radical C₃H₃ may combine directly with atomic N to form acrylonitrile.

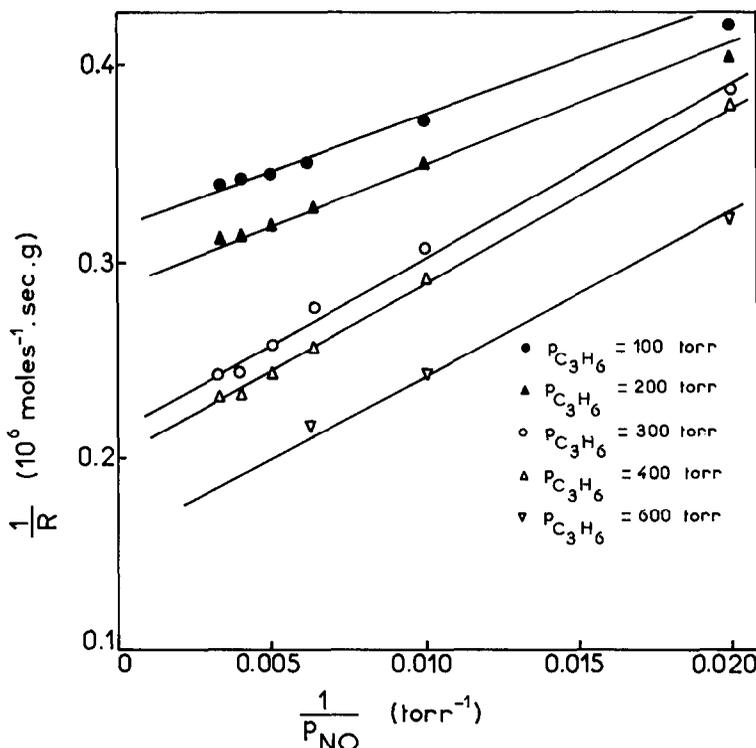


FIG. 10. Linear conversion (see text) of Fig. 6.

TABLE 4
 Values of k_r and k_o ^a

Constant	Reaction		Figures	
	(A) Disappearance of C ₃ H ₆ (mol/sec/Torr/g)	(B) Formation of C ₃ H ₃ N (mol/sec/Torr/g)	(A)	(B)
k_r	3.3×10^{-7}	3.5×10^{-8}	7	9
k_o	0.9×10^{-7}	7.5×10^{-8}	8	10

^a See text for details.

In a series of experiments made with acrolein and NO on a xerogel catalyst at 410°C, it was observed that an injection of ammonia, thus creating the conditions favoring the formation of imine, does not increase the selectivity into acrylonitrile as is shown by the first two lines of Table 5.

The absence of the imine step (13) is probably due to the nature of the catalyst (NiO-Al₂O₃) used in this work. Indeed, in an attempt to oxidize acrolein in the presence of ammonia, these conditions favoring the formation of imine and its oxidation (last line of Table 5), no traces of acrylonitrile are found, as is the case for the same mixture without ammonia (third line of Table 5). It then appears that on catalysts containing NiO, the formation of acrylonitrile implies the addition of atomic nitrogen to the C₃H₃ radical, without formation of imine and its oxidation. Conversely, a conventional catalyst of ammoxidation (Sb-Sn-O) used in a catalytic test at 410°C with a mixture

NO:C₃H₆:He = 1:5:4 gave the following selectivities: C₃H₃N, 29.2%; C₂H₃N, 9%; C₃H₄O, 33%; CH₃-CHO, 24.2%; CO₂, 4.4%. It behaves as a catalyst of partial oxidation of propylene by NO and not as a catalyst of formation of acrylonitrile.

Finally, Table 5 shows also that in the formation of acrylonitrile from propylene and NO acrolein is not involved. Indeed, the first line of this table shows that 27.5% of the initial acrolein is completely oxidized in the presence of NO. The low selectivity to acrylonitrile (13%) shows that in the reaction between propylene and NO (where the selectivity to acrylonitrile is of the order of 80%) the formation of acrolein is not an intermediate step. However, its formation may lead to the total oxidation of propylene. Indeed, when acrolein is added to a mixture of C₃H₆-NO-He, the selectivity S_{CO₂} (total oxidation) increases, indicating that the acrolein is oxidized over the catalyst. It is also probable that acrolein leads to some other

 TABLE 5
 Reactions of Acrolein

Mixture	Composition	Selectivity (%)					
		CH ₃ -CHO	C ₂ H ₄	C ₂ H ₃ N	C ₃ H ₃ N	C ₃ H ₆ O	CO ₂
NO:C ₃ H ₄ O:He	1:2.5:4.1	12	19	13.5	13	15	27.5
NO:C ₃ H ₄ O:He:NH ₃	1:2:4:2	12	19	15	12	15	27
O ₂ :C ₃ H ₄ O:He	1:2.5:4:1	15	12	0	0	8	65
O ₂ :C ₃ H ₄ O:He:NH ₃	1:2:4:2	13	9	0	0	7	71

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