

Some Aspects of Autoignition Delays and Flammability Limits of Polyurethane Based on Diphenyl Methane Diisocyanate (MDI) and Propoxylated Trimethylol Propane*

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Synopsis

The main purpose of this work is a better understanding of the physicochemical phenomena involved during an unpiloted ignition. We intend to characterize the step corresponding to the degradation of the material, the production of combustible gases, and their combustion with the surrounding oxidizing gas, leading to the flame. The degradation gases which are essentially alkanes, alkenes, and aldehydes undergo oxidation by degenerate chain branching mechanism. The initiating chain propagates very quickly and creates intermediate species of increased stability which initiate new active centers leading to secondary chains. Then, ignition can occur after a relatively large induction period. We suggest that this period may be defined as the time to reach a critical rate of production of the intermediate species. A study of the active center distribution near the surface as a function of time and of the distance to the surface allows us to explain the experimental variation of ignition delays vs. oxidant pressure. The ignition limits of this polyurethane, i.e., temperature–pressure curves in air and in oxygen, have also been determined. It has been possible to correlate pressure and temperature and to specify the influence of nitrogen on the ignition process.

INTRODUCTION

Polyurethane foams are widely used in buildings, as upholstery fillings and interior furnishings. Owing to their commercial and industrial interest and the importance of their behavior when involved in fire, their thermal degradation and ignition have to be studied thoroughly. Our investigations in this way concern a polyurethane based on diphenyl methane diisocyanate (MDI) and propoxylated trimethylol propane. The main purpose of this work is a better understanding of the physicochemical phenomena involved during an unpiloted ignition: ignition delays and limits.

As the heat source for ignition of materials, hot air and thermal radiation are often used. In the first case, air acts not only as a heat source but also as an oxidizer, in the second we have only a heat source. The simplest criterion for ignition by radiation is given by a solid thermal model where ignition occurs at the moment when the surface temperature of solid polymers has reached a critical value. It is considered that mixing and reaction between gaseous pyrolysis products and surrounding air are faster than the

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heat-up of material. Therefore, the phenomenon is merely controlled by a heat conduction process in the solid.

This model was applied by many investigators. Good surveys were published by Martin,¹ Welker,² and Kanury.³ However, this model does not include pyrolysis and thermal and chemical processes in the gas phase, which is a significant defect. Thus, Ohlemiller and Summerfield,⁴ measuring the ignition delays of epoxy resin under intense radiation flux, showed that the delay depends also on total and partial pressure of the ambient oxidizer.

A more general model, including chemical and thermal processes in both the gas and solid phases, has been proposed by Kashiwagi.⁵ In this model, it is assumed that the pyrolysis products of the polymer move in the opposite direction to the diffusion of ambient oxygen and flaming ignition occurs spontaneously in the mixing region of both components.

Ignition of natural and synthetic polymers in hot air and by thermal radiation plays an important role with respect to the cause of actual fires. These ignition processes are quite similar to the case of radiative ignition except that the heating mode for ignition includes also a convective one. Early studies of the ignition of polymers were performed with cellulosic materials in electrical furnaces. Observations and analyses of the ignition behavior given by Bamford et al.,⁶ Fons,⁷ Akita,⁸ and Weatherford and Sheppard⁹ are some examples.

In this paper, we used this type of experimental device and we intend to give a better characterization of the step corresponding to the degradation of the material, the production of combustible gases and their combustion with the surrounding oxidizing gas, leading to the flame.

We show that degradation gases which are alkanes, alkenes, and aldehydes undergo oxidation by degenerate chain branching mechanism, leading to a relatively large induction period before ignition. We suggest that this period may be defined as the time to reach a critical rate of production of the intermediate species, more stable, created by the initiating chain. A study of the spatial and temporal distribution of these species near the surface allows us to explain the experimental variation of ignition delays versus oxidant pressure.

The ignition limits of the polyurethane have also been determined. Then we try to correlate pressure and temperature and to specify the influence of nitrogen on the ignition process.

EXPERIMENTAL AND RESULTS

Few studies on ignition have been carried on polyurethanes. Moreover, the concerned authors have used experimental devices very different from ours.

As far as we are concerned, we have considered the spontaneous ignition process which gives quite reproducible results. This process can be defined as the appearance of the flame after the material has been quickly put into a hot oxidizing gas. This method had previously been performed in our laboratory by Breillat et al.¹⁰ The reactor they have built was described in their paper.

Measure of Autoignition Delays. Influence of Pressure

An experimental test consists of putting quickly into the reactor a sample of material which was at room temperature and to measure the time elapsed until the occurrence of flaming ignition.

The temperature of the reactor T_{∞} can be raised up to 750°C. The air pressure can be fixed from 0.2 up to $3 \cdot 10^5$ Pa. The samples we used are small cubes of 60 mg. To obtain results with a better accuracy, each value is the average result of 10 tests. The results we obtained as a function of air pressure and for different reactor temperatures are plotted in Figure 1.

Determination of Autoignition Limits. Influence of Nitrogen

It is possible to delineate on a pressure-temperature plane the ignition from nonignition zone. These curves have been obtained with air and with pure oxygen in order to consider the influence of nitrogen.

The curves have been delineated using the same experimental device as for the measure of delays. For a fixed pressure, the temperature is decreased in steps of 5°C until no more flaming ignition could be observed. Thus the limit is obtained with an accuracy of $\pm 5^\circ\text{C}$. The autoignition limits in air and pure oxygen are plotted on Figure 2.

ANALYSIS OF RESULTS

Autoignition Delays

Ignition is a result of the combustion of pyrolysis products of the polymer mixing with ambient oxygen moving in the opposite direction.

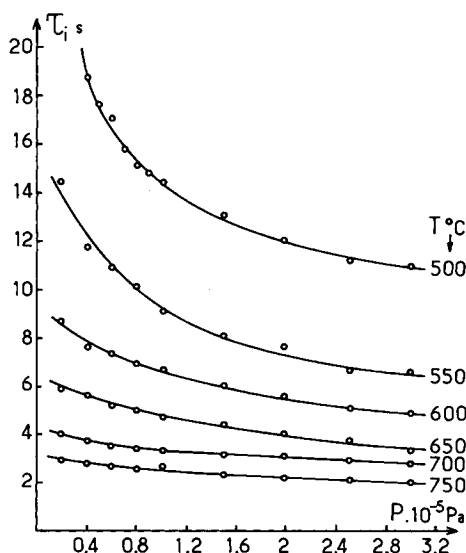


Fig. 1. Autoignition delays as a function of air pressure for different reactor temperatures.

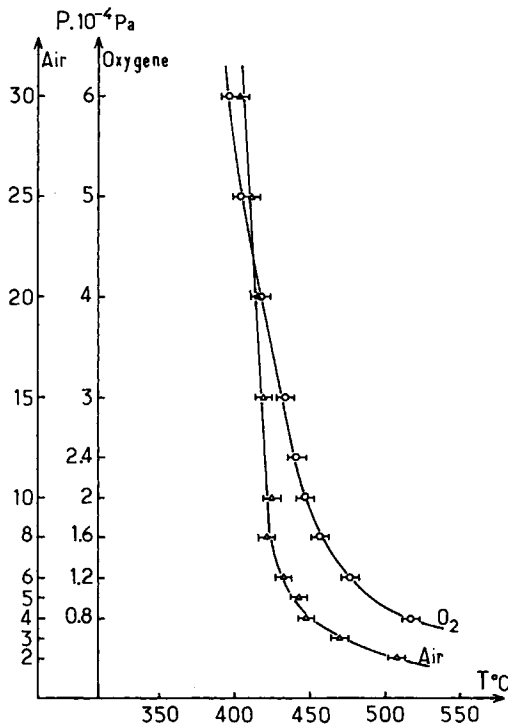


Fig. 2. Autoignition limits in air and pure oxygen.

So two steps can be distinguished in the measured delay τ_i :

(1) τ_h corresponding to the heating of the material from room temperature up to the temperature of the beginning of surface degradation;

(2) τ_c corresponding to the degradation of the material producing a gaseous phase and to the combustion of this phase leading to ignition. This is the "real" delay of combustion.

Determination of τ_h

The temperature of beginning of degradation of the studied polyurethane has been determined from dynamic TGA curves, analysis of degradation gases at various temperatures during the heating rise,^{11,12} and the study of the influence of oxygen pressure on this temperature. The value deduced is 250°C.

The delays τ_h have been evaluated by means of the differential equation governing the conservation of energy:

$$\rho_s c_{ps} \frac{\partial T}{\partial t} = k_s \nabla^2 T + \nabla I_r \quad (1)$$

with ρ_s density of material (kg m^{-3}), c_{ps} heat capacity [$\text{J (kg }^\circ\text{C)}^{-1}$], k_s thermal conductivity [$\text{W (m }^\circ\text{C)}^{-1}$], and I_r radiant flux (W m^{-2}), applied to our samples.

In this equation, the term ∇I , represents the contribution of interior absorption of radiation. Experimentally, we have been able to show that this absorption is negligible (the material is opaque).

So eq. (1) reduces to

$$\frac{\partial T}{\partial t} = \alpha_s \nabla^2 T$$

with

$$\alpha_s = \frac{k_s}{\rho_s c_{ps}} \text{ thermal diffusivity (m}^2 \text{ s}^{-1}\text{)}$$

which is Fourier's law of conduction.

We have to resolve this equation for a 3-dimensional system (our samples have a cubic shape). It is known that, to obtain the solution, it is possible to combine the solutions of 1-dimensional problems.¹³

So the solution can be generated by the common points in the mutually perpendicular intersection of two infinite slabs of thickness twice the edge of the cube and one infinite slab of thickness four times the edge of the cube. These calculations are detailed in a previous paper.¹⁴

To perform it, applied to our material, it has been necessary to determine its following physical properties:

heat capacity c_{ps} : $1.46 \times 10^3 \text{ J (kg } ^\circ\text{C)}^{-1}$;

thermal conductivity k_s : $0.27 \text{ W (m } ^\circ\text{C)}^{-1}$;

thermal diffusivity α_s : $2.12 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$.

The results show that τ_h is only a small fraction of the global delay τ_i , i.e., less than 12%.

T_∞ ($^\circ\text{C}$)	500	550	600	650	700	750
τ_h (s)	2.0	1.2	0.8	0.5	0.4	0.2

Theoretical Exploitation of the Step τ_c

We evaluate the delay τ_c subtracting the calculated value τ_h from the experimentally measured delay τ_i .

The polyurethane was thermally degraded by using the techniques of pyrolysis and TGA. Analysis and identification of pyrolysis products showed that the gaseous phase is essentially constituted by eight species: methane, carbon dioxide, ethylene, ethane, propene, propane, ethanal, and propanal.^{11,12} It is the oxidation of these compounds (except CO_2) which leads to ignition by radical mechanism.

However, we can prove that alkanes, alkenes, and aldehydes undergo oxidation by a single mechanism: degenerate chain branching reactions and linear breaking down of radicals. The initiating chain propagates very quickly and creates intermediate species more stable which initiate new active centers leading to secondary chains. Then ignition can occur after a relatively large induction period.

We suggest that this period τ_c , which corresponds really to the combustion step, may be defined as the time to reach a critical rate of production of the intermediate species. For degenerate chain branching reactions, the real active centers are these intermediate species, called U in this paper.

If n is the U concentration, it is well known that its evolution as a function of time is given by the following word statement:

$$\frac{dn}{dt} = \left[\begin{array}{l} \text{rate of U production} \\ \text{by initiating chain} \end{array} \right] + \left[\begin{array}{l} \text{rate of U production} \\ \text{by ramification} \end{array} \right] - \left[\begin{array}{l} \text{rate of U} \\ \text{breaking} \end{array} \right]$$

Let f denote the rate constant of U ramification, g the rate constant of homogeneous destruction and D_U the diffusion coefficient of U. The consumption of combustible gases by the very fast initiating step (whose rate is noted v_i) leading to the formation of ν molecules of U by the initiating chain has a rate $v = v_i\nu$. Each active center U being able to create η new radicals, the rate of U production by ramification is $f(\nu\eta - 1)n$. The rate of U homogeneous breaking is $g \cdot n$ and the rate of U heterogeneous breaking at the surface of the material may be written $D_U d^2n/dx^2$.

Then the general equation giving the variations of the U active center concentration as a function of time is the following:

$$\frac{dn}{dt} = v_i\nu + [f(\nu\eta - 1) - g]n + D_U \frac{d^2n}{dx^2} \quad (2)$$

This equation is integrable only if the values of v , f , and g can be considered as constant. This requires that the concentrations of the reactants be constant too. This also expects that the increase of temperature at and near the surface of the material does not produce a significant increase of these three factors.

It is not easy to predict the evolution of the temperature; however, we can consider that the material degradation which is an endothermic process absorbs an important fraction of the heat flux at the surface and lowers the evolution of the material temperature at and near the surface.

On the other hand, we know that before self-acceleration of the reaction the evolution of intermediate species U develops without a noticeable heat generation and so without a very marked increase of temperature.

At last, since a large rate of evolution of these species is required to obtain ignition, we may actually assume that the variation of v , f , and g are negligible during the combustion delay τ_c in comparison to the variations of n . Thus eq. (2) is integrable, v , f , and g being considered a constant.

Before ignition, the concentration of combustible gases is maximum in the vicinity of the surface. Thus ignition starts in this zone, and propagates afterwards in the adjacent gaseous layers.

Let us consider a very thin reaction zone adjacent to the surface, whose thickness is ϵ ; the distance $x = \epsilon$ corresponds to the maximum of reactivity.

We have to integrate eq. (2) on ϵ with the following boundary conditions: at $x = 0$, i.e., at the surface, the breaking steps are predominant and $n = 0$; at $x = \epsilon$, $dn/dx = 0$.

Let us write the homogeneous ramification factor $f(v\eta - 1) - g$ as the usual notation φ . It must be positive since the parametric conditions of pressure-temperature which were used lead to ignition. Equation (2) becomes

$$\frac{dn}{dt} = v + \varphi n + D_U \frac{d^2n}{dx^2} \tag{3}$$

The solution of (3) is a function of two variables: time t and distance x from the surface. Let us call $n_{(x,t)}$ this solution. It may be obtained using a classical method of variable separation, in the form of an expansion series.

At first, we have to search for a solution independent of time and which verifies the boundary conditions. Let us denote it n_0 :

$$n_0 = \frac{v}{\varphi} \left(\cos \frac{\varphi}{D_U} x + \frac{\sin[(\varphi/D_U)\epsilon]}{\cos[(\varphi/D_U)\epsilon]} \sin \frac{\varphi}{D_U} x - 1 \right)$$

Next, we develop it into a Fourier series expansion: we have two possibilities: expand it on an interval $0-\epsilon$ with a discontinuity when $x = \epsilon$; expand it on an interval $0-2\epsilon$ without discontinuity. The latter case is more appropriate because the convergence of the solution is more certain. So n_0 can be written

$$n_0 = \sum_{n=1}^{\infty} a_n \sin \frac{n\pi x}{2\epsilon}$$

which is a Fourier sine series expansion whose coefficient a_n is given by

$$a_n = \frac{1}{\epsilon} \int_0^{2\epsilon} n_0 \sin \frac{n\pi x}{2\epsilon} dx$$

This leads to the solution

$$n_0 = - \frac{4v}{\pi D_U} \sum_{k=0}^{\infty} \frac{\sin(2k + 1) \pi x / 2\epsilon}{(2k + 1) [\varphi / D_U - (2k + 1)^2 \pi^2 / 4\epsilon^2]} \tag{4}$$

with $n = 2k + 1$, because only the odd values of n are possible.

Next we seek a complete solution of equation (3) $n_{(x,t)} = n_1 + n_0$, n_1 being the solution of (3) without the constant term v ; hence

$$\frac{dn_1}{dt} = \varphi n_1 + D_U \frac{d^2n_1}{dx^2} \tag{5}$$

The initial conditions involve $n_{1(x,0)} = -n_0$ and the boundary conditions $n_{1(0,t)} = 0$ and $n_{1(2\epsilon,t)} = 0$. Solving eq. (5) by the classic method of variable separation, writing $n_1 = f(x) \cdot g(t)$, n_1 becomes

$$n_1 = \sum_{n=1}^{\infty} B_n \sin \frac{n\pi x}{2\epsilon} \exp\left(\varphi - D_U \frac{n^2\pi^2}{4\epsilon^2} t\right)$$

The initial condition $n_{1(x,0)} = -n_0$ gives

$$-n_0 = \sum_{n=1}^{\infty} B_n \sin \frac{n\pi x}{2\epsilon}$$

Hence

$$\begin{aligned} n_1 = & \frac{4v}{\pi D_U} \sum_{k=0}^{\infty} \frac{\sin(2k+1)\pi x/2\epsilon}{(2k+1) [\varphi/D_U - (2k+1)^2\pi^2/4\epsilon^2]} \\ & \times \exp\left[\varphi - \frac{(2k+1)^2\pi^2 D_U}{4\epsilon^2} t\right] \end{aligned} \quad (6)$$

By combining (4) and (6), the exact solution for the intermediate species distribution is obtained:

$$\begin{aligned} n_{(x,t)} = & \frac{4v}{\pi} \sum_{k=0}^{\infty} \frac{\sin(2k+1)\pi x/2\epsilon}{(2k+1) [\varphi - (2k+1)^2\pi^2 D_U/4\epsilon^2]} \\ & \times \left\{ \exp\left[\varphi - \frac{(2k+1)^2\pi^2 D_U}{4\epsilon^2} t\right] - 1 \right\} \end{aligned}$$

This function is defined in the interval $0-2\epsilon$ and is periodic (period 2ϵ). Its derivative is continuous on this interval. So we know that the Fourier series converges to the function on each continuity point.

The evolution of the intermediate species concentration versus time is maximum at $x = \epsilon$. The governing expression is

$$\frac{dn_{(\epsilon,t)}}{dt} = \frac{4v}{\pi} \sum_{k=0}^{\infty} \frac{\exp[\varphi - (2k+1)^2\pi^2 D_U/(2k+1)] t}{2k+1}$$

or

$$\begin{aligned} \frac{dn_{(\epsilon,t)}}{dt} = & \frac{4v}{\pi} e^{\varphi t} \left(\frac{\exp(-\pi^2 D_U/4\epsilon^2)}{1} + \frac{\exp(\dots)^9}{3} \right. \\ & \left. + \frac{\exp(\dots)^{25}}{5} + \dots \right) \end{aligned}$$

As ϵ is very small, $\exp(-\pi^2 D_U/4\epsilon^2)$ is small relative to 1. Thus it appears that the terms of the sum become rapidly small, and the second is already negligible relative to the first.

Limiting the series to the first term ($k = 0$), we can consider that a satisfying expression of the derivative is given by

$$\frac{dn_{(\epsilon,t)}}{dt} = \frac{4v}{\pi} \exp\left(\varphi - \frac{\pi^2 D_U}{4\epsilon^2} t\right)$$

The combustion delay τ_c corresponds to the time necessary to reach a sufficiently large rate of intermediate species production.

There is no noticeable generation of heat and increase of temperature in the reaction zone during this interval of time; but once this sufficiently large rate is reached, the reaction self-accelerates very quickly, resulting in combined autocatalytic and thermal effects. The rate of energy release in the reaction zone is much greater than the rate of heat loss; thus, the temperature rises, increasing more and more the heat generation.

We define the combustion delay τ_c as the time needed to reach a given arbitrary critical value of the ratio of the rate of intermediate species evolution to the initiating rate v :

$$\left[\frac{dn_{(\epsilon,t)}/dt}{v} \right]_{cr} = \frac{4}{\pi} \exp\left(\varphi - \frac{\pi^2 D_U}{4\epsilon^2} t\right) \tau_c$$

This ignition criterion implies that the product of τ_c and the net branching factor ($\varphi - \pi^2 D_U/4\epsilon^2$) is a constant. It can be noted that this relation is similar to the well-known one established in homogeneous kinetics.

Taking into account the complexity of the oxidation process for the different combustible gases, the φ term may be expressed as a function of pressure in the following manner:

$$\varphi = AP^m$$

where m is the global order of the ramification and homogeneous destruction process. Moreover, as the diffusion coefficients vary inversely with pressure and it can be assumed that ϵ is fairly constant, we have to verify experimentally a relation of the form

$$\tau_c \left(AP^m - \frac{B}{P} \right) = C = \text{const}$$

or

$$\frac{P}{\tau_c} = \frac{1}{C} (AP^{m+1} - B)$$

From the experimental results obtained by varying the air pressure at a constant temperature (cf. Fig. 1), we can effectively verify the preceding linear relation (Fig. 3), m being close to a mean value of 0.27. On this figure, the straight lines cross at a negative but close to zero ordinate value ($B/C \approx 0.0014 \times 10^5 \text{ Pa s}^{-1}$), which does not appear clearly on the graph despite the scale used. This involves $C \gg B$ and $A > B$; nevertheless, it is difficult to go further because A , B , and C values are not available.

Let us note that, for each measurement of the delay at various pressures, the initiating rate v changes because it is pressure-dependent. However, the preceding relation remains valid because the chosen ignition criterion concerns a critical ratio of the rates of formation and initiation of species U.

Autoignition Limits

Examining Figure 2, we can observe that nitrogen has a promoting effect on normal autoignition for pressures under $2 \times 10^5 \text{ Pa}$. We have seen that the processes leading to autoignition involve branching chain reactions and that chain carriers can be deactivated in two ways: they can diffuse to the surface or they can be destroyed in the homogeneous phase by recombination of atoms and radicals. These recombination reactions are strongly exothermic and frequently require a third body to dissipate released energy.

At low pressure, the diffusion of active species is easier and heterogeneous deactivation prevails. At higher pressure, bi- and trimolecular collisions are favored, and homogeneous deactivation is dominant. At lower pressures, nitrogen slows down the diffusion of chain carriers towards the sample surface, reduces their heterogeneous deactivation and consequently promotes normal autoignition. As pressure increases, nitrogen contributes to dissipate the excess of energy of the recombination reactions and partici-

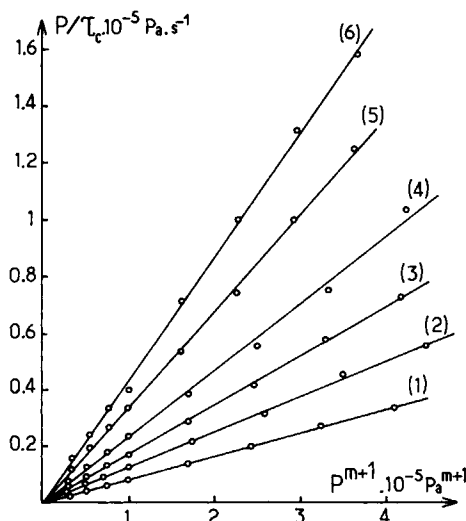


Fig. 3. Variation of the ratio P/τ_c as a function of P^{m+1} for the various studied temperatures. T ($^{\circ}\text{C}$), m : (1) 500, 0.28; (2) 550, 0.36; (3) 600, 0.30; (4) 650, 0.31; (5) 700, 0.17; (6) 750, 0.18.

pates in the homogeneous deactivation of chain carriers. This inhibitor effect competes with the promoting one and we can see, on the autoignition diagram, that these two effects compensate at a pressure about 2×10^5 Pa. Further, the limits are practically superimposed, with or without nitrogen.

It has been seen that the ramification factor φ can be expressed in the concise manner $\varphi = AP^m$. Let us denote φ^* as the net branching factor $\varphi - B/P$; introducing the normal Arrhenius preexponential term A^* and the global activation energy E , it can be written as

$$\varphi^* = A^*P^m \exp(-E/RT) - B/P \quad (7)$$

By writing φ^* in this form, the influence of temperature on the diffusion coefficient is not taken into account. The first term of (7) depends on temperature exponentially; hence, we can neglect the variation of the second term with T in comparison to the variation of the first.

The autoignition limit corresponds to the transition between the steady state ($\varphi^* < 0$) and the self-accelerated process ($\varphi^* > 0$); then, at the limit $\varphi^* = 0$ and (7) gives

$$A^*P^m \exp(-E/RT) = B/P$$

or

$$\ln P = C' + E/(m + 1)RT \quad (8)$$

Another approximation is to replace the reaction zone temperature T with the reactor temperature T_∞ ; they are close near the limits. Taking into account these approximations, and plotting $\ln P$ vs. $1/T$ (Fig. 4), the relation (8) is well verified for the entire field of pressure with pure oxygen and until about 0.8×10^5 Pa with air.

In the latter case, it seems that beyond this pressure the competition previously noted between promoting and inhibiting effect of nitrogen disturbs the phenomena and changes the activation energy of the chain mechanism.

Excluding this parametric field, the two straight lines are parallel with a mean slope $E/(m + 1)R$ of 9540 K. So the following value for the global activation energy can be obtained:

$$E = 1.01 \times 10^5 \text{ J mol}^{-1}$$

CONCLUSION

This paper has been concerned with the study of ignition delays and limits of a polyurethane based on MDI and propoxylated trimethylol propane. We have measured delays and determined the autoignition limits, studying the influence of temperature and pressure on them.

We have considered that the measured delay τ , could be divided in two steps: a heating step followed by a combustion step. The heating delay τ_h has been evaluated by solving numerically Fourier's law of conduction

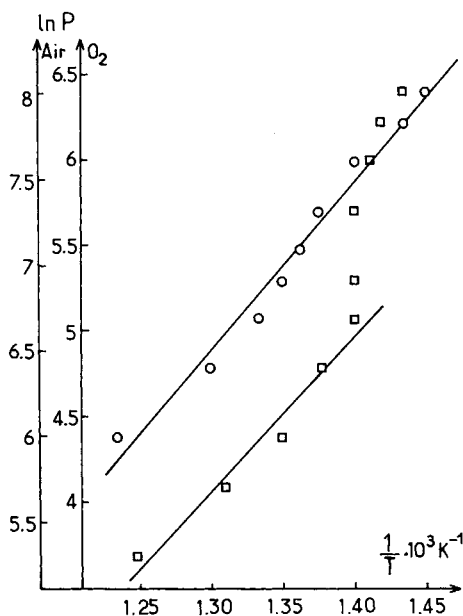


Fig. 4. Logarithm of pure oxygen (○) and air pressure (□) vs. reciprocal absolute temperature.

applied to the used samples (cubes of small size). Thus it has been shown that for these samples, the first step is short in comparison to the global delay τ_i .

Next we have tried to explain theoretically the second step or "true" combustion delay $\tau_c (= \tau_i - \tau_h)$. This delay corresponds to the self-accelerated oxidation by degenerate chain branching mechanism of gaseous species diffusing from the solid.

It is hypothesized that τ_c is the time required to reach a critical rate of production of intermediate species. A spatial and temporal study of the active center distribution near the surface of the material allows us to show that ignition delay is inversely proportional to the ramification factor of the global reaction, a relation similar to the one encountered in homogeneous combustion. Experimentally, it has been possible to verify this relation between autoignition delays and oxidant pressure.

Next we have delineated the autoignition limits in air and in pure oxygen; the influence of nitrogen has been specified. As the limit corresponds to a zero value of the net branching factor, it has been possible to correlate pressure and temperature. A value of the global activation energy has been deduced from it.

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