

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Kinetics of the Non-explosive and Explosive Reaction between Hydrogen and Oxygen Sensitized by Nitrogen Peroxide. II^{1,2}

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For the explosion condition in the nitrogen peroxide-sensitized reaction between hydrogen and oxygen both the thermal⁵ and the isothermal branched chain^{6,7} explanations have been proposed. It will be shown in this paper that it is difficult to satisfy the requirements of the thermal theory by any specific reaction mechanism and that such difficulties do not exist for the isothermal branched-chain theory which, therefore, is to be preferred over the former.

Thermal Interpretation of Explosion Condition.—In the thermal theory the explosion condition can be derived from the simplified, but for this purpose adequate, equation for the net rate of heat production

$$dq/dt = Anpfe^{-E/RT} - K(T - T_0) \quad (1)$$

where the first term on the right side is the rate of production of heat by the reaction and the second term the rate of loss by conduction. The latter is proportional to the difference between the temperatures T inside and T_0 outside the vessel. The reaction rate is proportional to the number of collisions between chain carriers and reactants. The chain-carrier concentration is n , and the concentration of reactants is proportional to the total pressure p and a mixture ratio factor f . If for $dq/dt = 0$ equation (1) has a real root in T there will be a steady state. But if for fixed values of the other constants n is increased sufficiently the equation will have no real root, and dq/dt will always be positive. The maximum value of n which gives a real root is the critical value at the boundary between the explosive and non-explosive regions. Taking K independent of pressure, then if f is approximately

constant it is seen from equation (1) that this critical value of n must be approximately inversely proportional to the pressure. If there are gradients of concentration n and of temperature in the vessel, the condition of ignition will be first established in some element of volume of highest temperature and concentration, but equation (1) is still approximately valid.

An important restriction is imposed on the thermal theory by the observation⁵ that the upper and lower critical nitrogen peroxide concentrations (U. C. C. and L. C. C., respectively) are unaffected by light, whereas the induction periods are greatly shortened. There seems to be only one general mechanism in the thermal theory that can explain these facts. This mechanism was proposed by Foord and Norrish,⁵ as follows: (a) the reaction is of the branched-chain type and light accelerates only the rate of chain initiation θ ; (b) the branching factor ϕ in the equation

$$dn/dt = \theta + (\alpha - \beta)n = \theta + \phi n \quad (2)$$

(where n is the chain-carrier concentration and α and β are the coefficients of chain branching and chain breaking, respectively) is a quadratic function of the nitrogen peroxide concentration and is positive over substantially the whole range of catalytic activity of nitrogen peroxide; (c) at high chain-carrier concentrations self-neutralization of the chain carriers establishes a steady state provided that thermal equilibrium can be maintained throughout the entire volume; (d) at this steady state the production of chain carriers by the branching mechanism is much faster than by the initiating mechanism, so that the equation

$$n_e = \phi/\delta \quad (3)$$

is valid, where n_e is the equilibrium concentration of chain carriers and δ is the coefficient of the self-neutralization reaction. If n_e exceeds some critical value, explosion occurs.

Since δ can be considered constant over the whole range of catalytically effective nitrogen peroxide concentrations and since the thermal properties of the mixture and, therefore, the critical n_e are nearly identical at the U. C. C. and

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior, and the Director, Coal Research Laboratory, Carnegie Institute of Technology. (Not subject to copyright.)

(2) Part I, von Elbe and Lewis, THIS JOURNAL, **59**, 2022 (1937).

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(5) Foord and Norrish, *Proc. Roy. Soc. (London)*, **A152**, 196 (1935).

(6) Thompson and Hinshelwood, *ibid.*, **A124**, 219 (1929).

(7) Hinshelwood and Williamson, "The Reaction between Hydrogen and Oxygen," Oxford Press, New York, N. Y., 1934.

the L. C. C., it is seen from equation (3) that $\phi_U = \phi_L$ where the subscripts U and L refer to values at the U. C. C. and L. C. C., respectively. The induction period τ is obtained by integrating equation (2) between the limits $n = 0$ and $n = n_c$

$$\tau = \frac{1}{\phi} \ln \left(\frac{\phi}{\theta} n_c + 1 \right) \quad (4)$$

where n_c ($< n_c$) is the critical concentration of chain carriers at the end of the induction period where the reaction becomes fast. n_c is regarded as constant, and since θ_L is smaller than or at best equal to θ_U (from consideration of initiating mechanism, reactions (1), (2) and (3) below; see also first term of equation (7)) it follows that $\tau_L \geq \tau_U$. Experimentally it was found that $\tau_L < \tau_U$, and it is therefore necessary to assume that the true L. C. C. is lower and that the experimental L. C. C. is found at a higher nitrogen peroxide concentration due to some secondary process. This point will be discussed later in connection with the isothermal branched-chain treatment where a similar result is found. It can be demonstrated that any specific reaction mechanism in which ϕ is a quadratic function of (NO_2) will describe satisfactorily the trend of the induction periods. For plausible displacements of the L. C. C., absolute values of the coefficients of branching and breaking reactions can be calculated from which activation energies can be estimated (by means of the Arrhenius equation), whose values appear to be reasonable.

Thus far no objections to the theory are apparent. However, difficulties arise on attempting to fit a specific reaction mechanism to the observations of the effect of pressure and mixture composition on the U. C. C. In any mechanism, ϕ , in the upper range of catalytically effective nitrogen peroxide concentrations, is of the form

$$\phi = f(y)[a - by] \quad (5)$$

where $y = (\text{NO}_2)$ and $f(y)$ is a function of an order smaller than 1. Since the upper limit of catalytic activity of nitrogen peroxide (where $\tau = \infty$) is approximately determined by

$$a = by \quad (6)$$

and since experiments show⁵ that this limiting concentration is only a little larger than the U. C. C., it follows that a is only a little larger than by_U , and ϕ , in the neighborhood of the U. C. C., becomes enormously sensitive to any experimental variable that varies a or b independently. Considering changes of total pres-

sure and remembering that the critical n_c is approximately inversely proportional to the total pressure (see equation (1)), it follows that ϕ_U/δ is also approximately inversely proportional to the total pressure. If self-neutralization involves a third body δ is proportional to the pressure and $\phi_U = \text{constant}$. If the predominant chain carriers are polyatomic radicals like HO_2 or NO_3 which can react with themselves in binary collisions, δ is independent of and ϕ_U inversely proportional to the pressure. If, now, a specific reaction mechanism is chosen by which a in equation (5) is proportional say to the first power and b independent of pressure, then for a two-fold increase in pressure a constant ϕ_U would demand a more than two-fold increase in y_U , and a ϕ_U varying inversely as the pressure an even larger increase in y_U . This is an impossible result, because y_U is thus increased to values far beyond the experimental limit of catalytic activity of NO_2 while actually y_U decreases with increasing pressure.⁶ Results of this kind are obtained with any mechanism that involves the reaction $\text{O} + \text{H}_2 = \text{OH} + \text{H}$, together with the regeneration of oxygen atoms by reactions between chain carriers and reactants, among which may be mentioned $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, $\text{HO}_2 + \text{NO}_2 = \text{HNO}_3 + \text{O}$ and $\text{HO}_2 + \text{NO}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{NO} + \text{OH} + \text{O}$. An example is the mechanism proposed by Foord and Norrish.^{5,8} In part I of this investigation it was shown that oxygen-atom mechanisms of this type are ruled out on the basis of the isothermal branched-chain theory of the explosion limit. The same conclusion is now reached on the basis of the thermal theory.

The foregoing demonstrates that, on the basis of the thermal theory, a workable mechanism must yield a and b as pressure functions of about the same order. A similar requirement exists with respect to the dependence of these terms on mixture composition; otherwise changes of the latter would produce extreme displacements of the U. C. C. which are not consistent with experimental data, although it must be admitted that the observations are erratic and somewhat inconclusive on this point. It seems to be quite impossible, however, to find a plausible specific reaction mechanism that at once satisfies the requirements of variations in pressure and mixture composition, and this constitutes a serious difficulty for the thermal interpretation.

(8) Cf. Norrish, *THIS JOURNAL*, **60**, 1513 (1938).

Isothermal Branched-Chain Interpretation of Explosion Condition.—The isothermal branched-chain theory allows the selection of a specific reaction mechanism^{2,9} using Thompson and Hinshelwood's⁶ studies of the explosion limits, which mechanism is also consistent with the analysis of the unsensitized reaction between hydrogen and oxygen.^{2,9,10} However, it has not been extended⁸ to the observations of Norrish and Griffiths¹¹ and Foord and Norrish⁵ on the induction periods in the sensitized non-explosive and explosive reaction. This will be done in the following paragraphs.

1. Pressure Effect at the End of the Induction Period in the Non-explosive Reaction.—If nitrogen peroxide is added in amounts smaller than the L. C. C. and larger than the U. C. C. a non-explosive reaction takes place. Two phases precede this non-explosive reaction: an induction period during which a very small decrease of pressure occurs, followed by a small but sharp increase of pressure which, after passing through a maximum, decreases sharply again. If nitrogen peroxide is added in amounts between the L. C. C. and U. C. C. the induction period is followed by an explosion.

The end of the induction period is marked by a rise in temperature because this is the only way in which a development of pressure can occur in a reaction that proceeds with a decrease in the number of molecules. In a quiescent mixture the increase in temperature must be greater at the center of the vessel for two reasons: first, heat conduction; and, second, the chain-carrier concentration is greatest at the center of the vessel, since chains are destroyed at the wall. Thus, taking the rate of formation of water proportional to the product $(H_2)(OH)$ (see below), one may conceive of the growth of the OH concentration at the center of the vessel to a critical value at which thermal equilibrium will no longer be maintained.¹² If the sudden thermal effect is localized at the center of the vessel, the subsequent retardation may be attributed to convection currents that are set up in the quiescent mixture. With the rates of heat dissipation and chain breaking at the surface thus considerably increased, the system is able to reach a steady state.

(9) Lewis and von Elbe, "Combustion, Flames and Explosions of Gases," Cambridge University Press, 1938.

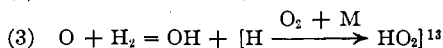
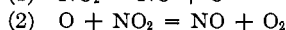
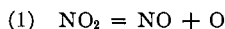
(10) Von Elbe and Lewis, *THIS JOURNAL*, **59**, 656 (1937).

(11) Norrish and Griffiths, *Proc. Roy. Soc. (London)*, **A139**, 147 (1933).

(12) That the transition from practically isothermal to non-isothermal conditions can occur in a narrow critical range of reaction rates is shown by the work of Rice, Allen and Campbell [*THIS JOURNAL*, **57**, 2212 (1935)].

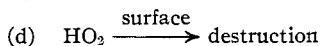
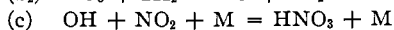
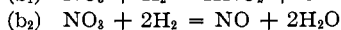
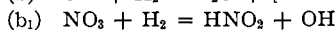
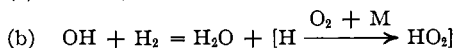
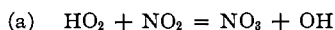
2. Induction Period as a Function of Nitrogen Peroxide Concentration.—When induction periods both inside and outside the explosion region are plotted against partial pressures of nitrogen peroxide, they are found to fall on a continuous curve of the form indicated by the experimental points in Fig. 1. The curve exhibits a minimum induction period within the explosion region between the L. C. C. and U. C. C.

An equation of the form of (2) in which θ , α and β appear as functions of nitrogen peroxide concentration can be obtained from the specific reaction mechanism referred to above² after introducing a chain-initiating mechanism. Following Foord and Norrish this may be assumed to consist of



The oxygen-atom concentration reaches a steady state rapidly and the rate of production of chain carriers OH and HO₂ is given by $K = 2k_1k_3(H_2)(NO_2)/(k_2(NO_2) + k_3(H_2))$. K may be considered reasonably constant over most of the range of catalytically effective nitrogen peroxide concentrations since the rate coefficient of reaction 2 is much larger than that of reaction 3.¹⁴

The rest of the reaction mechanism, retaining the previous² equation designations, follows



Development of differential equations of the type of equation 2 for each of the three chain carriers OH, HO₂ and NO₃ encounters prohibitive difficulties. However, OH is efficiently removed in the gas phase by reaction b, and it appears justified to assume the condition of the steady state for this chain carrier during the induction period. Concerning HO₂ use may be made of the fact that the unsensitized reaction between hydrogen and oxygen above the upper limit proceeds at a steady state rate with practically no induc-

(13) At the temperatures and pressures employed in studies of the sensitized reaction, the reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ is almost completely suppressed in favor of $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$. This is demanded by the analysis^{9,10} of the unsensitized reaction at the upper explosion limit.

(14) Schumacher, *THIS JOURNAL*, **52**, 2584 (1930).

tion period. According to the theory,^{9,10} this means that reaction d proceeds rapidly enough under the conditions obtaining to ensure the establishment of the steady state. In the present case reaction d is even faster because of the smaller density; moreover, reaction a, by which HO₂ is also removed, must proceed even faster than d according to relationships obtained for the critical concentrations^{2,9}; in addition, the great length of the induction period here suggests that the rate of chain initiation is a slower process than in the unsensitized reaction. From these considerations it appears justified to extend the assumption of the steady state condition to HO₂. This limits the problem to the development of the concentration of NO₃ as a time function which leads to the equation

$$\frac{d(\text{NO}_3)}{dt} = \frac{K}{2} \frac{1 + 2k_b(\text{H}_2)/k_c(\text{M}) (\text{NO}_2)}{1 + k_d k_b(\text{H}_2)/k_a k_c(\text{M}) (\text{NO}_2)^2} + \frac{k_{b_1}(\text{H}_2)^2}{(\text{NO}_2)^2 + k_d k_b(\text{H}_2)/k_a k_c(\text{M})} \left[(\text{NO}_2) \left(\frac{k_{b_1} k_b}{k_{b_2} k_c(\text{M})} - \frac{k_d}{k_a} \right) - (\text{NO}_2)^2 - \frac{k_d k_b(\text{H}_2)}{k_a k_c(\text{M})} \right] (\text{NO}_3) \quad (7)$$

In deriving this equation it is assumed as in the previous paper² that $k_{b_1}(\text{H}_2)^2 \gg k_{b_1}(\text{H}_2)$. This assumption requires, on the basis of the expression for the L. C. C., that $k_a(\text{NO}_2) \gg k_d$ over practically the entire range of catalytically effective nitrogen peroxide concentrations. In equation 7 the first term is θ and the second term is ϕn of equation 2.

Equation 7 must be integrated between the limits of zero time and a time, τ , at which the reaction proceeds fast enough to produce a temperature rise. No formal consideration of the temperature equilibrium can be included in the treatment and the critical condition can only be expressed by stating that the rate of consumption of reactants has reached some critical value. Since the initiating mechanism consumes reactants only at a negligible rate and since the hydrogen-consuming reactions b_1 and b_2 are subordinate to b , this critical condition is reached when the rate of reaction b equals $k_b(\text{H}_2)(\text{OH})_c$. The thermal properties of the mixture are not appreciably affected by a few per cent. of nitrogen peroxide, so that this critical rate and, therefore, $(\text{OH})_c$ may be regarded constant over the whole range of catalytically effective nitrogen peroxide concentrations making the equation for the induction period applicable over this whole range.

The relation between $(\text{NO}_3)_c$ and $(\text{OH})_c$ is given by

$$(\text{NO}_3)_c = [k_b(\text{H}_2)(k_d/k_a(\text{NO}_2)) + k_c(\text{M})(\text{NO}_2)](\text{OH})_c/k_{b_1}(\text{H}_2) - K/k_{b_1}(\text{H}_2) \quad (8)$$

Let $y = (\text{NO}_2)$. Since the explosion condition is $\phi_{U,L} = 0$ the bracketed factor of ϕ in equation 7 is equal to $(y_U + y_L)y - y^2 - y_U y_L$. Hence, $k_d k_b(\text{H}_2)/k_a k_c(\text{M}) = y_U y_L$. Let $k_{b_1}(\text{H}_2) = b_1$, $k_{b_2}(\text{H}_2)^2 = b_2$, $2k_b(\text{H}_2)/k_c(\text{M}) = m$ and $k_c(\text{M})(\text{OH})_c/K = r$. Then

$$b_1/b_2 = \frac{2}{m} (y_U + y_L + 2y_U y_L/m) \quad (9)$$

$$\theta = \frac{K}{2} (1 + m/y)/(1 + y_U y_L/y^2) \quad (10)$$

$$\phi = b_2((y_U + y_L)y - y^2 - y_U y_L)/(y^2 + y_U y_L) \quad (11)$$

$$n_c = (\text{NO}_3)_c = 2Km(ry - 1 + y_U y_L r/y)/b_2(y_U + y_L + 2y_U y_L/m) \quad (12)$$

At the U. C. C. and L. C. C. equation 4 reduces to $\tau_U = n_{c(U)}/\theta_U$ and $\tau_L = n_{c(L)}/\theta_L$. Then

$$m = (y_U \tau_U - y_L \tau_L)/(\tau_L - \tau_U) \quad (13)$$

$$r = b_2 \frac{(y_U + y_L + 2y_U y_L/m)(y_U - y_L)\tau_U \tau_L}{(y_U \tau_U - y_L \tau_L)(y_U + y_L)^2} + \frac{1}{y_U + y_L} \quad (14)$$

The equation for τ is obtained by substituting equations 10 to 14 in equation 4. For numerical calculations experimental values of τ_U , τ_L , y_U and y_L and one pair τ , y from the data of Foord and Norrish must be introduced, thus providing a value of b_2 . Since m must be positive, equation 13 demands that $\tau_L \geq \tau_U$. This makes it necessary to assume, as in the thermal theory, that the true L. C. C. is lower than the experimental L. C. C. A possible explanation for this displacement of the L. C. C. may be inferred from the remarks (under 1) on the pressure effect that follows the induction period in the non-explosive reaction. If, in the incipient explosion, convection currents are set up, the rate of chain breaking at the surface is considerably increased, and, as may be seen from equation (9) in the previous paper,² the L. C. C. would be particularly sensitive to this pressure effect. Of interest in this connection is the remark of Thompson and Hinshelwood⁶ that the lower limit tended to drift in a rather indefinite way, depending on vessel conditions. The increase of surface chain breaking due to gas motion furnishes, in many instances, an explanation for differences in the results of kinetic studies in static and flow experiments.

If τ_L is assumed to approach τ_U closely ($y_L = 0.094$ mm.; $y_U = 0.506$ mm.; $\tau_U = 55.5$ seconds) and a pair of values τ , y is chosen close to the minimum of the experimental points, the curve

in Fig. 1 is calculated which agrees reasonably well with the experimental points. The condition $\tau_L = \tau_U$ corresponds to a value of $b_1/b_2 = 0$. If $\tau_L = 1.18 \tau_U$ ($y_L = 0.083$ mm.), $b_1/b_2 = 0.53$ and the calculated curve remains practically unchanged. Since a ratio of b_1/b_2 larger than this is inconsistent with the effect of pressure on the U. C. C. this provides a limit to the displacement of the L. C. C.

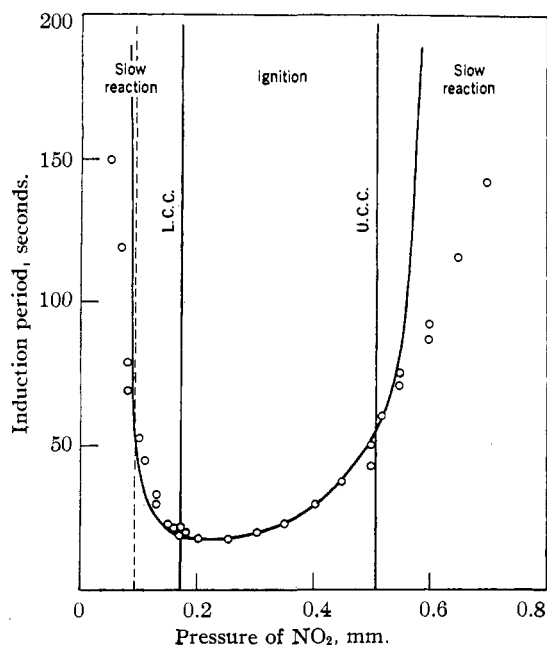


Fig. 1.—Curve of induction period vs. partial pressure of NO_2 . \circ , Foord and Norrish's experimental values at 357° for $(2\text{H}_2 + \text{O}_2) = 151$ mm.; —, calculated curve (equations 4 and 10 to 14); solid lines are experimental L. C. C. and U. C. C.; dotted line is displaced L. C. C.

The order of magnitude of b_2 remains the same between the above limits of displacement of the L. C. C., namely, from 0.140 to 0.412 sec.^{-1} as τ_L is increased. Using the method of Tolman¹⁵ and the experimental data (see Fig. 1) the distance of approach δ of the molecules NO_3 , H_2 and H_2 for the trimolecular reaction is calculated to be $\delta = 3 \times 10^{-10 - E/2880}$, which is sufficiently small compared with molecular diameters and admits of an energy of activation E of several thousand calories.

In the theory as presented in both this and the previous paper² it is implicitly assumed that the temperature rise does not interfere seriously with the trend of the critical concentrations found by Thompson and Hinshelwood. This may ac-

(15) Tolman, "Statistical Mechanics," A. C. S. Monograph, 1927, pp. 245-250.

count for the fact that the experimental values of both limits have been found to be somewhat erratic.

3. Suppression of Explosion by Internal Surface.—On inserting a glass rod in the center of the reaction vessel the explosive reaction may be suppressed, giving way to a fast non-explosive reaction whose rate reaches a maximum at some nitrogen peroxide concentration intermediate between the former critical concentrations.

It can be reasonably supposed that by the insertion of a rod the rate of chain breaking is increased to such an extent that the branching factor ϕ always remains negative. Under such conditions the steady state reaction rate corresponding to the mechanism given in this paper exhibits a maximum at a nitrogen peroxide concentration lying between the former critical concentrations. This is perhaps sufficiently evident to make further elaboration unnecessary.

In another place⁹ it was suggested that there may exist second-order chain-breaking processes which would allow the reaction to reach a steady state at high chain-carrier concentrations, that is, high reaction rates, if isothermal conditions could be maintained. This latter may be approximately accomplished by the rod. Instead of the explosion region there now appears a region of fast reaction with a maximum rate between the former critical concentrations. However, there seems to be no necessity for considering second-order chain-breaking processes.

4. Effect of Light.—The insensitivity of the critical concentrations toward light which dissociates NO_2 into NO and O is to be expected, since only the initiating mechanism is accelerated, leaving the explosion condition $\phi = 0$ unchanged. The effect of the light intensity I on the induction period (for the displacement $\tau_L = \tau_U$) is described by the equation

$$\tau = \frac{1}{\phi} \ln \left[\frac{4\phi (y + y_U y_L / y) (y + y_U y_L / y - 1/r)}{b_2 (y_U + y_L)} r + 1 \right] \quad (15)$$

where $r = k_c(M) (\text{OH})_c / (K + aI)$. With this equation and an appropriate value of constant a the experimental curve of τ vs. I determined by Foord and Norrish¹⁶ can be reproduced. For $1/r = y + y_U y_L / y$, $\tau = 0$; so that for sufficiently large light intensities τ remains zero up to the highest catalytically effective nitrogen peroxide concentrations and becomes finite only below

(16) Ref. 5, Fig. 4, p. 205.

some small nitrogen peroxide concentration. This corresponds rather well with the observations of Foord and Norrish.¹⁷

5. Induction Periods and Explosion Limits with Varying Oxygen and Inert Gas Pressures.—As has been stated in Part I² of this investigation, the third body in reaction c must be either O₂ or inert gas. The rate of reaction d is governed by diffusion and is therefore proportional to 1/(M). ϕ thus becomes a quadratic function of both the concentrations of O₂ and inert gas. On varying, for instance, the O₂ pressure and keeping the H₂ and NO₂ pressures constant, two explosion limits are obtained, and the induction periods follow a curve similar to that shown in Fig. 1 in agreement with the observations of Foord and Norrish.¹⁸ Furthermore, Foord and Norrish⁵ have established the existence of an upper explosion limit for added N₂ and A. The experiments were not carried to the range where the lower explosion limit is expected to appear.

(17) Ref. 5, Fig. 3, p. 204.

(18) Ref. 5, Fig. 6, p. 207.

Summary

If the explosion condition is formulated on the basis of the thermal theory it is not possible to find any plausible specific reaction mechanism that describes the effect of pressure and mixture composition on the upper critical NO₂ concentration. This includes the mechanism proposed by Foord and Norrish.

In a previous publication, the isothermal branched-chain theory was used to derive a specific reaction mechanism consistent with the trend of the critical concentrations. This mechanism is now extended to describe the observations of Foord and Norrish on the induction periods in the explosive and non-explosive reaction and related observations. This furnishes a complete description of the experimental data and thus allows a decision to be made in favor of the isothermal branched-chain theory of explosion.

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Utilization of Aryloxy Ketones in the Synthesis of Quinolines by the Pfitzinger Reaction¹

BY PAUL K. CALAWAY^{2,3} WITH HENRY R. HENZE

Although the utilization of aldehydes and ketones in the synthesis of quinoline derivatives has been studied frequently, no attempt appears to have been made to use keto ethers in this manner. We have been interested in the possibility of converting such substituted ketones into substituted quinoline acids which might have value as anti-malarials.

The availability of isatin and of four aryloxy ketones suggested employing the method of Pfitzinger⁴ in the production of cinchoninic acids with substituents in the 2- or 2,3-positions. Through this procedure from an unsymmetrical ketone, RCH₂COCH₂R', two isomeric products might be

obtained, the mechanism of reaction having been formulated as shown.⁵

Thus, while the utilization of methyl ethyl ketone has resulted chiefly in the production of 2,3-dimethylcinchoninic acid,^{4c} the simultaneous formation of 2-ethylcinchoninic acid has been established.⁶ Since the keto ethers available were aryloxyacetones, no experience was at hand from which to predict with certainty whether the chief product of their reaction, by means of the Pfitzinger procedure, would be the 2-aryloxy-methyl or the 2-methyl-3-aryloxy-cinchoninic acid.

We have studied the condensation of isatin with phenoxyacetone, α - and β -naphthoxyacetone and thymoxyacetone, respectively. The product in each instance has been shown to be the 3-aryloxy-4-quinolinecarboxylic acid. The

(1) Presented before the Division of Organic Chemistry at the 97th meeting of the American Chemical Society at Baltimore, Md., April 3-7, 1939.

(2) From the Ph.D. dissertation of Paul K. Calaway, June, 1938.

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(4) Pfitzinger, (a) *J. prakt. Chem.*, **33**, 100 (1886); (b) *ibid.*, **38**, 582 (1888); (c) *ibid.*, **56**, 283 (1897).

(5) Halberkann, *Ber.*, **54**, 3090 (1921).

(6) Von Brauu, Gmelin and Schultheiss, *ibid.*, **56**, 1344 (1923).