them have been indicated. The pressure values obtained agree with those of Keyes within experimental error.

2. The dissociation pressures of potassium deuteride have been measured by the same method from 270 to 360°. The dissociation pressure of potassium deuteride is approximately twice as great as that of potassium hydride throughout the temperature range studied.

3. From equations connecting the dissociation pressure with the temperature, the following heats of formation per mole have been calculated: for potassium hydride, 14,150 calories; for potassium deuteride, 14,450 calories. The difference is hardly greater than the experimental error.

4. A possible method for the separation of hydrogen and deuterium has been suggested.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Kinetics of the Explosive Reaction between Hydrogen and Oxygen Sensitized by Nitrogen Peroxide[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

Small traces of nitrogen peroxide exert a remarkable influence on the combination of hydrogen and oxygen, inducing explosions at temperatures where the gases alone are almost completely inert to each other, far below the temperature corresponding to the tip of the hydrogen–oxygen explosion peninsula.[4,5] At any such temperature there exist two sharply defined critical concentrations of nitrogen peroxide between which instantaneous inflammation of the hydrogen and oxygen takes place but above or below which there is only a slow reaction.

Experimental investigation of the phenomenon reveals the following facts.[5] At a given temperature and mixture composition the lower critical concentration (L. C. C.) is raised and the upper critical concentration (U. C. C.) is lowered as the pressure of the hydrogen–oxygen mixture is increased. If the total pressure is kept constant the U. C. C. is lowered on increasing the proportion of oxygen to hydrogen; it is also lowered by the presence of nitrogen. Results on the effect of nitrogen on the L. C. C. are meager; the effect does not seem to be pronounced. Increasing temperature lowers the L. C. C. and raises the U. C. C. As the temperature is decreased the effect of total pressure on the L. C. C. becomes less pronounced. The U. C. C. is much the same in silica as in porcelain vessels. The L. C. C. tends to drift in a rather indefinite way but the difference in the two kinds of vessels is not very great. It will be helpful for the ensuing discussion to reproduce the table[5] of critical concentrations.

TABLE I

CRITICAL CONCENTRATIONS OF NITROGEN PEROXIDE IN A STOICHIOMETRIC MIXTURE OF HYDROGEN AND OXYGEN AT DIFFERENT TEMPERATURES AND PRESSURES

Temp., °C.	Pressure of NO_2, mm.							
	Lower critical concentration				Upper critical concentration			
	150	300	450	600	150	300	450	600
410	0.053	0.076	0.107	0.144	>9.9	7.9	4.4	3.1
390	.068	.09	.122	.160	4.6	2.7	1.8	1.3
370	.09	.12	...	.15	1.47	0.98	0.59	0.39

Apparently these nitrogen peroxide pressures were not corrected for the equilibrium between nitric oxide and nitrogen peroxide.[4,6] This correction, though affecting the absolute values, does not alter the trend appreciably. The revised values, for example, for 410° are

L. C. C.	0.032	0.053	0.079	0.010
U. C. C.	>6.1	5.5	3.2	2.4

Thus, at this temperature, the L. C. C. and the U. C. C. are roughly proportional and inversely proportional, respectively, to the total pressure. As the temperature is decreased the U. C. C. remain approximately inversely as the pressure, while the L. C. C. tend to become independent of pressure.

The foregoing facts forcibly suggest the occurrence of a branched chain reaction initiated in

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[2] Coal Research Laboratory, Carnegie Institute of Technology.

[3] Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[4] Dixon, Gibson and Hinshelwood, *Trans. Faraday Soc.*, **24**, 559 (1928).

[5] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **A122**, 610 (1929); *ibid.*, **A124**, 219 (1929).

[6] For this equilibrium consult Zeise, *Z. Elektrochem.*, **42**, 785 (1936).

some way by nitrogen peroxide. It was proposed early[7] that O atoms, formed by the dissociation of nitrogen peroxide in a collision with an energy-rich molecule, branched according to

$$O + H_2 = OH + H \qquad (I)$$

At the L. C. C. this induced branching would become equal to the rate of chain breaking. The following chain breaking reaction was assumed to occur

$$NO_2 + O = NO + O_2 \qquad (II)$$

An O atom could, therefore, either branch by (I) or be destroyed by (II). Since the probability of the latter increases with increasing nitrogen peroxide concentration, an upper critical value ultimately should be reached. Objections to this mechanism are twofold. First, there is strong evidence that (II) is so much faster than (I)[8] (at least 10^4 times faster at room temperature and 10^2 times faster at 400°) that in the presence of even small amounts of nitrogen peroxide (I) would be suppressed. Secondly, attempts to find a mechanism based on O atoms that could describe the above facts have been unsuccessful.[9] A solution of the problem and also the difficulties of an oxygen atom mechanism will be demonstrated by developing alternative mechanisms on the basis of chemical plausibility and then investigating their kinetic consequences. The heats of reactions in Table II will be helpful in following the discussion.

TABLE II

HEATS OF REACTIONS INVOLVING OXIDES OF NITROGEN

$NO + O = NO_2 + 71.5$ kcal.
$H + NO_2 = HNO_2$ (gas) + 74 kcal. (very approx.)
$OH + NO_2 = HNO_3$ (gas) + 36.5 kcal.
$N_2O_4 + O = N_2O_5 + 60$ kcal.

The kinetic problem consists of assigning to nitrogen peroxide the dual role of participant in branching and breaking reactions,[10] the latter to become predominant over the former toward higher concentrations of nitrogen peroxide. The normal branching reaction

$$H + O_2 = OH + O \qquad (III)$$

is unimportant under the conditions of these experiments, being entirely suppressed by the reaction[11]

$$H + O_2 + M = HO_2 + M \qquad (IV)$$

It must, therefore, be supposed that on collision of nitrogen peroxide with a chain carrier X, branching may occur. Branching need not take place directly in this reaction but an intermediate compound may be formed which is capable of producing chain carriers by further reaction with the molecules of the reactants. X could be identified with one of the four chain carriers, O, OH, HO_2 and H.[11] In view of reaction (II) branching between nitrogen peroxide and O is impossible. For energetic reasons the reaction between nitrogen peroxide and OH is restricted to association; likewise, the resulting product nitric acid could not react with hydrogen to produce chain carriers. There remain only HO_2 and H for each of which only two plausible reactions that meet the above requirements may be formulated. If

$$HO_2 + NO_2 = NO_3{}^{12} + OH \qquad (V)$$
$$HO_2 + NO_2 = HNO_3 + O \qquad (Va)$$
$$H + O_2 + NO_2 = NO_3 + OH \qquad (VI)$$
$$H + O_2 + NO_2 = HNO_3 + O \qquad (VIa)$$

the bond energy of the third O atom in NO_3 is not larger than the corresponding bond energy in N_2O_5, then the reaction

$$NO_3 + H_2 = HNO_2 + OH \qquad (VII)$$

is exothermic to the extent of about 17 kcal. Reactions V or VI and VII constitute one branching possibility; the other consists of reactions Va or VIa and I. It is now necessary to introduce a breaking reaction involving nitrogen peroxide. In case O atoms are formed, one is rather strongly committed to II, but in any case the choice of an alternative will not prove to be advantageous. If V or VI is operative, the obvious reaction is

$$OH + NO_2 + M = HNO_3 + M \qquad (VIII)$$

A chain breaking reaction between nitrogen peroxide and HO_2 need not be considered for energetic reasons, and the reaction $H + NO_2 + M = HNO_2 + M$ is entirely overshadowed by IV due to the relative magnitudes of the concentrations of nitrogen peroxide and oxygen.

Thus, essentially the following two alternative mechanisms result from the above considerations:

Mechanism A

a $X + NO_2 \longrightarrow NO_3 + OH$
b $OH + H_2 \longrightarrow X$
b_1 $NO_3 + H_2 \longrightarrow OH$
b_2 $NO_3 \longrightarrow$ destruction
c $OH + NO_2 \longrightarrow$ destruction
d $X \longrightarrow$ destruction

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[7] Schumacher, *Z. physik. Chem.*, **B10**, 7 (1930).

[8] Schumacher, THIS JOURNAL, **52**, 2584 (1930).

[9] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, p. 308.

[10] Hinshelwood and Williamson, "The Reaction between Hydrogen and Oxygen," Oxford Press, 1934.

[11] Von Elbe and Lewis, THIS JOURNAL, **59**, 656 (1937).

[12] For the isolation and properties of NO_3 see Schwarz and Achenbach, *Ber.*, **68**, 343 (1935); *cf.* Lemon and Lowry, *J. Chem. Soc.*, 1409 (1936); Gmelin's "Handbuch der anorganischen Chemie," 8th Edition, 1935; Schumacher, *Z. anorg. Chem.* **233**, 47 (1937).

Mechanism B

a′ $X + NO_2 \longrightarrow O$
b′ $O + H_2 \longrightarrow 2X$
c′ $O + NO_2 \longrightarrow$ destruction
d $X \longrightarrow$ destruction

From mechanism A the equation for the critical concentrations of NO_2 is

$$(NO_2)^2 - \left[\frac{k_{b_1}(H_2)}{k_{b_1}(H_2) + k_{b_2}} \frac{k_b(H_2)}{k_c} - \frac{k_d}{k_a}\right](NO_2) + \frac{k_bk_d}{k_ak_c}(H_2) = 0 \quad (1)$$

Mechanism B gives

$$(NO_2)^2 - \left[\frac{k_b'}{k_c'}(H_2) - \frac{k_d}{k_a'}\right](NO_2) + \frac{k_b'k_d}{k_a'k_c'}(H_2) = 0 \quad (2)$$

The lower and upper critical concentrations may be written with good approximation by neglecting the first and third terms, respectively, in these equations, since the L. C. C. is much smaller than the U. C. C. except at lower temperatures. From (1)

$$(NO_2)_{\text{lower}} = \frac{k_bk_d(H_2)}{\frac{k_{b_1}(H_2)}{k_{b_1}(H_2) + k_{b_2}} k_ak_b(H_2) - k_ck_d} \quad (3)$$

$$(NO_2)_{\text{upper}} = \frac{k_{b_1}(H_2)}{k_{b_1}(H_2) + k_{b_2}} \frac{k_b}{k_c}(H_2) - \frac{k_d}{k_a} \quad (4)$$

From (2)

$$(NO_2)_{\text{lower}} = \frac{k_b'k_d(H_2)}{k_a'k_b'(H_2) - k_c'k_d} \quad (5)$$

$$(NO_2)_{\text{upper}} = \frac{k_b'}{k_c'}(H_2) - \frac{k_d}{k_a'} \quad (6)$$

Suitable commitments about the individual reactions must now be made to make these equations conform to the experimental facts. For equations (5) and (6) (mechanism B) this proves to be a hopeless task. As far as the effect of pressure is concerned, the best that can be done is to make the U. C. C. decrease with pressure by assuming both d and c′ to involve three body collisions—a rather implausible assumption for c′. It is evident by inspection of (6) that this would not describe the experimental inverse proportionality of the U. C. C. with pressure; and by inspection of (5) it is seen that it would cause the L. C. C. always to increase with a power of the pressure greater than 1. There do not seem to be acceptable variations of mechanism B, as, for example, the inclusion of reactions b and c of mechanism A, that would lead to a better description of the critical concentrations.

Equation (4) has the advantage that reaction c already involves a three body collision (reaction VIII). It remains, therefore, to determine b_1 and b_2 so that $k_{b_1}(H_2)/(k_{b_1}(H_2) + k_{b_2})$ becomes inversely proportional to the pressure. Since b_1 is identified with the binary reaction VII, b_2 should be a ternary reaction and proceed at a rate that considerably exceeds b_1. The obvious choice is

$$NO_3 + 2H_2 = NO + 2H_2O \quad (IX)$$

It must be assumed that IX, which is highly exothermic, occurs at almost every triple collision whereas VII has a high energy of activation. Since the U. C. C. decreases on increasing the proportion of oxygen to hydrogen, the third body in reaction c must preferably be oxygen or an inert gas like nitrogen. This would be differentiated sufficiently from the reaction in which hydrogen is the third body, if with the latter a chain continuing reaction instead of chain breaking occurred, namely

$$OH + NO_2 + H_2 = NO + H_2O + OH \quad (X)$$

If X is identified with H atoms then reaction d becomes IV and the critical concentrations, as determined from reactions VI, XI, the latter being

$$OH + H_2 = H_2O + H \quad (XI)$$

VII, IX, VIII and IV (representing in order the six reactions in mechanism A), are

$$(NO_2)_{\text{lower}} = \frac{k_4k_{11}(H_2)\,(M)}{\frac{k_6k_7k_{11}}{k_9} - k_4k_8(M)^2} \quad (7)$$

$$(NO_2)_{\text{upper}} = \frac{k_7k_{11}}{k_8k_9}\frac{1}{(M)} - \frac{k_4(M)}{k_6} \quad (8)$$

If X is identified with HO_2, reaction d becomes

$$HO_2 \xrightarrow{\text{surface}} \text{destruction} \quad (XII)$$

and the H atoms are removed by IV. Similarly, the critical concentrations are now determined from reactions V, XI, VII, IX, VIII and XII.

$$(NO_2)_{\text{lower}} = \frac{k_{11}k_{12}}{\frac{k_5k_7k_{11}}{k_9} - k_8k_{12}}\frac{(H_2)}{(M)} \quad (9)$$

$$(NO_2)_{\text{upper}} = \frac{k_7k_{11}}{k_8k_9}\frac{1}{(M)} - \frac{k_{12}}{k_5(M)} \quad (10)$$

k_{12} depends on the vessel dimensions and to some extent on the nature of the surface.

The foregoing two sets of equations (7), (8) and (9), (10) can be brought into complete harmony with the experimental facts if it is assumed that the X = HO_2 mechanism predominates at lower temperatures and the X = H mechanism at higher temperatures and that the negative terms in (8) and (10) are unimportant. The first of these assumptions seems reasonable if it is granted that a competition exists between VI and

$$H + O_2 + NO_2 = HNO_2 + O_2 \quad (XIII)$$

VI coming into prominence at higher temperatures because of its larger energy of activation. Therefore, at low temperatures the L. C. C. is independent of pressure and depends on vessel conditions. Unfortunately, no experiments are available in this range on the effect of inert gases or change of mixture composition. With increasing temperatures both mechanisms overlap. The full expression for the composite mechanism is complicated but it suffices to state that the consequence would be a gradual increase in the pressure dependence of the L. C. C. with increasing temperature. One would expect the approximate linear dependence at 410° to be replaced by a dependence of even higher order at still higher temperatures. However, the phenomena become more involved at higher temperatures as the reactions that determine the normal explosion limits of hydrogen and oxygen come into play. The almost negligible effect of nitrogen on the L. C. C. at an intermediate temperature, 395°, found in an isolated experiment,[5] might be taken to indicate the overlapping of the two mechanisms. The second of the above assumptions makes the U. C. C. inversely proportional to the pressure and independent of surface conditions as demanded by the experimental data for the ranges of temperature and pressure investigated. Remembering that (M) in the positive terms of (8) and (10) represents only concentrations of oxygen and inert gases, it is evident that an increase of the percentage of oxygen or addition of inert gas should decrease the U. C. C. The effect of temperature is given correctly by the equations for both the U. C. C. and L. C. C. The energies of activation of VII and XI far exceed those of VIII and IX; therefore, the U. C. C. will increase with increasing temperature. Since both IV and XII have little or no energy of activation, then by the same token the L. C. C. will decrease with increasing temperature.

Summary

The nitrogen peroxide-sensitized explosion of hydrogen and oxygen has been subjected to kinetic analysis. The evidence rules out a mechanism based on oxygen atoms and points to a mechanism in which NO_3, H, OH and HO_2 take part. Equations are developed for the lower and upper critical concentrations of nitrogen peroxide which satisfactorily account for the known experimental facts.

EXPLOSIVES DIVISION
PITTSBURGH EXPERIMENT STATION
U. S. BUREAU OF MINES, AND
COAL RESEARCH LABORATORY
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Kinetics of the Dry and Water-Catalyzed Reaction between Carbon Monoxide and Oxygen at and above the Upper Explosion Limit[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

Like mixtures of hydrogen and oxygen, mixtures of carbon monoxide and oxygen exhibit the phenomenon of the low pressure explosion peninsula.[4,5] The tip of the peninsula is at about 600° and the upper explosion limit extends upward from about 70 mm.; evidently the peninsula is in a considerably higher temperature and pressure region than the hydrogen-oxygen explosion peninsula. The position of the upper limit is practically uninfluenced by water vapor; it is independent of vessel size; it is shifted toward higher pressures on replacing carbon monoxide by oxygen and *vice versa*, but the effect is not marked; inert gases lower the upper limit in that they can replace to some extent either of the reactants—nitrogen is particularly striking, the $CO + O_2$ mixture being replaceable fairly exactly by equal amounts of nitrogen. On the other hand, the reaction above the upper limit is strongly accelerated by traces of water vapor and hydrogen, in the absence of which only a slow and predominantly heterogeneous reaction takes place.

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(2) Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

(3) Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

(4) Kopp, Kowalsky, Sagulin and Semenoff, *Z. physik. Chem.*, **B6**, 307 (1930).

(5) Hadman, Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **A137**, 87 (1932); **A138**, 297 (1932).