2. The results are discussed in an attempt to formulate generalizations for cyclopentanones analogous to those formulated for cyclohexanones by Woodward.[2]
3. The most important of such generalizations is that the conjugated *exo*-cyclic double bond in the cyclopentanones shifts the absorption maximum to the red from that of the corresponding cyclohexanones and in contrast to the shift to the blue of the conjugated *endo*-cyclic double bond in the cyclopentenones.

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[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND]

The Explosion of Nitrous Oxide–Hydrogen Mixtures

BY CHARLES P. FENIMORE AND JOHN R. KELSO

This paper presents explosive limits for the nitrous oxide–hydrogen system. When combined with Melville's[1] interpretation of his slow reaction data between these gases, the explosive data strongly indicate the presence of the radical HO_2 in the reacting system. Although a detailed reaction mechanism cannot be based on these findings, it is of some interest that the processes forming HO_2 occur at temperatures 200° or more higher in this system than they previously have been known to occur in other reaction systems.[2]

Since Melville encountered explosions in his studies of the slow reaction but did not observe reproducible limits, it is necessary to state at the outset that reproducible limits can be readily obtained. To do so, the gases must be oxygen-free, however, and their entry into the reaction vessel must be rapid. The second requirement is necessary presumably so that not much molecular oxygen can be formed by the thermal decomposition of nitrous oxide before the pressure builds up to the explosion limit. Hence, the second requirement is only a restatement of the first, that the gases must be oxygen free.

Experimental

Hydrogen and nitrous oxide, freed from oxygen by treatment with aqueous alkaline pyrogallol and dried, were mixed in a previously evacuated vessel in the desired proportions. Proportions were estimated by an attached mercury manometer. The mixing vessel communicated to the reaction vessel through a stopcock of 2-mm. bore. The reaction vessel was heated in an electric resistance furnace and fitted with two chromel alumel thermocouples whose readings did not differ by more than 1°. Adequate temperature constancy could be maintained through a Sorensen voltage regulator and variable transformers with only occasional manual control. Two cylindrical quartz reaction vessels 30 cm. long were used; one measured 0.9 cm. inside diameter, the other 2.5 cm. These two vessels were new and manufactured at the same time and place, and presumably possessed similar surfaces. In addition, runs were made in a cylindrical vycor vessel of 1.5 cm. inside diameter. The findings obtained in the vycor vessel showed the same features as those in quartz up to 830° and are not reported in detail.

After the mixing vessel had been filled at a pressure such that the pressure would rise to the desired value in the previously evacuated reaction vessel when the gas was partitioned between them, the stopcock was opened rapidly. An explosion ensued immediately or not at all. No perceptible induction period was ever noted. Explosions were indicated by a sharp click and a bright flash of light which propagated back through the stopcock into the mixing vessel. The color of the light was dependent on temperature and composition. Explosions at low temperatures or of compositions rich in hydrogen appeared reddish; those at higher temperatures or of mixtures rich in nitrous oxide yellowish or white. At 800° only compositions containing over 50% hydrogen appeared at all reddish.

At a given temperature and gas composition, observations were repeated at varying pressures until the lower pressure limit was bracketed within 1–2 mm. The measurements were taken over a fairly extended period of time and frequent returns to limits measured weeks or months before proved the values, at temperatures $\leqslant 830°$, reproducible to 3–5 mm. The results obtained in vycor between 900 and 980° were less reproducible ($\simeq \pm 10$ mm.).

Results and Discussion

In Figs. 1 and 2, the lower limiting explosion pressure for nitrous oxide–hydrogen mixtures is plotted as a function of temperature and gas composition for vessels of two different sizes. The decimal point serves a double purpose in these contour maps. In addition to pointing off tenths of a cm. of a pressure determination, each point places the temperature and composition at which that determination was made. At temperatures below 720° in the small vessel (or 670° in the larger one) the explosion pressure was too high to observe in a quartz and glass apparatus. For the same reason, the minimum explosion pressure escaped capture in either vessel above 820°. In a vycor vessel of 1.5-cm. inside diameter, very similar results

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[1] Melville, *Proc. Roy. Soc.* (London), **142A**, 524 (1933); **146A**, 737, 760 (1934).

[2] For a discussion and for references, see Minkoff, *Faraday Soc. Discussions*, **2**, 151 (1947).

were obtained; the explosive region extended from 670 to 820°, the minimum explosion pressure (6.6 cm.) occurred with 69% nitrous oxide at 740°.

The most striking feature of these data is that in any section of fixed composition the pressure *versus* temperature curve possesses a minimum; although if no change occurred in the reaction mechanism, a continuous decrease of the lower limit would be anticipated with increasing temperature. The nature of the reaction which intrudes to upset a steady decrease of the explosion limit becomes evident when a small amount of oxygen is added to the reactants. We have found oxygen to be an efficient poison for the explosive reaction, although Melville found it an effective catalyst for the slow reaction. Extensive tests proved that the addition of 2 mm. of oxygen raised the explosion limit above 20 cm. wherever it was less than this value in Figs. 1 and 2. This quantity of oxygen was much greater than the amount necessary to inhibit the reaction, however. Nitrogen was prepared containing 3% of oxygen, and it was found that the addition of 5 mm. of this mixture to the reactant gas drove the explosion pressure above 20 cm. for any composition at 780 and 820° in the large reaction vessel and at 760 and 800° in the smaller vessel.

The effect of added oxygen must be ascribed to the chemical nature of the additive since nitrogen (free from oxygen) did not inhibit the explosions. In general, the effect of 2–12 mm. of added nitrogen was to depress slightly or to leave unaltered the pressure of nitrous oxide plus hydrogen required for explosion. Added in still larger amounts, nitrogen increased the limiting pressure of the reactants. It might be conceived that the effect of oxygen could depend only on its paramagnetism and that nitric oxide would also inhibit the explosive reaction. This was proved false. The addition of 3 mm. of nitric oxide slightly shifted the minimum pressure toward the stoichiometric ratio, but left the main features of Fig. 1 unchanged.

The inhibition of explosions by added oxygen suggests an explanation for the existence of a minimum in the explosion limit in the absence of added oxygen. Nitrous oxide undergoes thermal decomposition to nitrogen and oxygen and the obvious conclusion is that at a high enough temperature the decomposition furnishes oxygen enough to inhibit the explosive reaction between nitrous oxide and hydrogen.

For a more detailed statement of this view, we consider the following sequence of reactions by which Melville interpreted his studies of the slow reaction and note that if these equations are valid

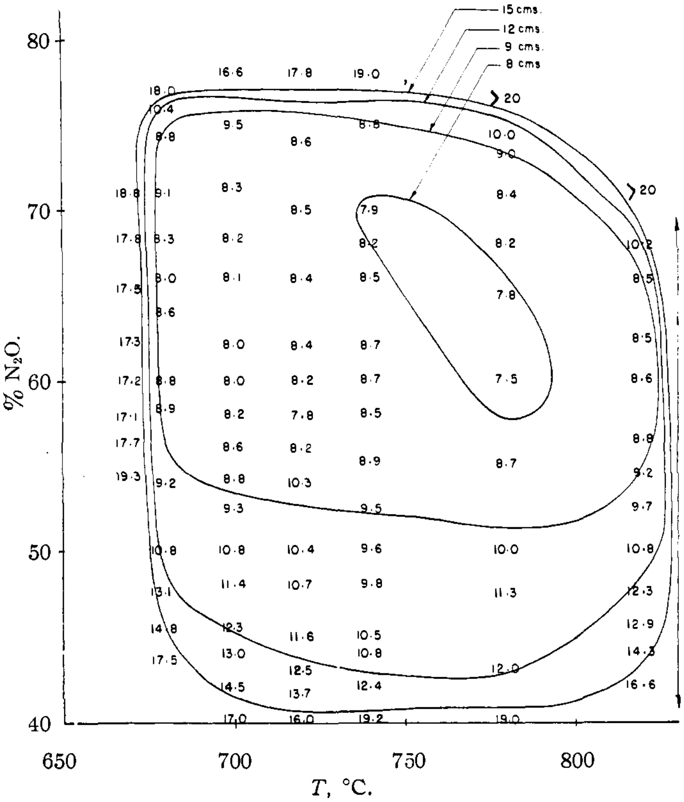

Fig. 1.—Lower explosion limit of N_2O–H_2 mixtures in 2.5-cm. i. d. quartz vessel.

$$N_2O \longrightarrow N_2 + O \quad (1)$$
$$O + H_2 \longrightarrow OH + H \quad (2)$$
$$H + N_2O \longrightarrow OH + N_2 \quad (3)$$
$$OH + H_2 \longrightarrow H_2O + H \quad (4)$$
$$H \longrightarrow \text{recombination on wall or third body} \quad (5)$$

for the explosive as well as for the slow reaction, it appears inevitable that the mechanism of poisoning by added oxygen must be

$$H + O_2 + M \longrightarrow HO_2 + M \text{ (}HO_2\text{ is inert)} \quad (6)$$

because the hydrogen atom is the only labile particle in Melville's sequence which could react with molecular oxygen. The natural assumption is that the inhibition of the explosive reaction even without added oxygen is also caused by (6), and this because nitrous oxide decomposes to give chiefly molecular oxygen and nitrogen, although the decomposition is not allowed for in Melville's sequence.

The success of (6) as a poisoning reaction is founded on the stability of HO_2 or, more precisely, on the fact that HO_2 is destroyed without the generation of free radicals which can re-enter the gas phase reaction. While this is the only fate permitted above, it is obvious that the reaction

$$HO_2 + H_2 \longrightarrow H_2O_2 + H \quad (7)$$

might proceed in the nitrous oxide–hydrogen system since it does so in the oxygen–hydrogen system where its occurrence permits the third explo-

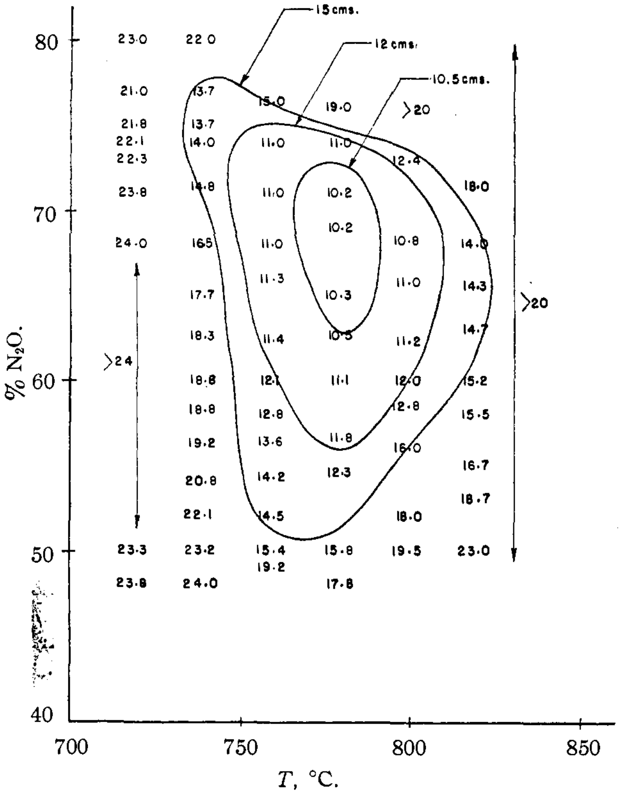

Fig. 2.—Lower explosion limit of nitrous oxide–hydrogen mixtures in 0.9-cm. i. d. quartz vessel.

sion limit.[3] A comparison of Figs. 1 and 2 hints that this reaction does in fact take place. In the larger vessel, the explosive region extends much farther toward hydrogen-rich mixtures than in the smaller vessel, while the limit toward nitrous-oxide-rich mixtures is only slightly extended. In view of the weak dependance of explosion pressure on vessel size (the minimum explosion pressure in the two vessels varies inversely with the cube root of the diameter) this strong feature could not result from a greater diffusion path alone. It might be expected, however, if reaction (7) occurred because the greater diffusion path to the wall allows greater opportunity for the regeneration of the hydrogen atom before destruction of the HO_2 radical at the wall in the larger than in the smaller vessel, and hence a greater extension of the explosive region toward hydrogen-rich mixtures is permitted.

It is of interest to ask whether HO_2 will remain a quasi-inert body as temperature is increased. In the absence of any major change of reaction mechanism, it would be expected that if HO_2 became unstable or more reactive at higher temperatures the explosion limit would decrease again because a chain-breaking mechanism would have ceased to operate. Furthermore, if such an effect were observed it should be accompanied by a cessation or at least a great diminution of the poisoning effect of added molecular oxygen. We have not been able to recapture the explosion limit in either of the quartz vessels between 830 (where it vanished) and 960°. In the vycor vessel, on the other hand, the explosion limit reappeared at 900° and slowly decreased as the temperature was raised further. At the higher temperatures (above 900°) the minimum explosion pressure occurred much nearer the stoichiometric ratio than in the lower temperature region. In Fig. 3, the explosion limit is plotted for equimolar mixtures in a 1.5-cm. inside diameter vycor vessel. The addition of 2 mm. of molecular oxygen to this mixture produced only a slight effect in the temperature range from 900 to 980° (increased the explosion pressure by an amount $\lessdot 10$ mm.) although the low temperature lobe was destroyed by a similar addition of oxygen, just as it was in either quartz vessel.

It will be recalled that the vycor vessel gave lower explosion limits than those obtained in even a larger quartz vessel in the low temperature range as well, $T < 830°$, and this may be due either to the greater facility of hydrogen atom recombination on quartz than on vycor or to a difference in the fate of HO_2 on quartz and on vycor. The first alternative appears the simpler, and it is probable that a more rugged or larger apparatus would allow the recapture of the explosion limit in quartz above 900°. The major constitutive difference between vycor and quartz is the presence of approximately 4% of boric oxide and small amounts of sodium, iron, aluminum and arsenic in the latter; and the larger quartz vessel was treated with boric oxide and with sodium borate in an attempt to force the reappearance of the explosion limit.

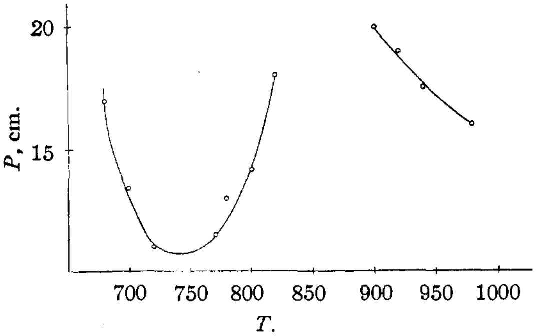

Fig. 3.—Lower explosion limit of 1:1 nitrous oxide–hydrogen mixtures in 1.5-cm. i. d. vycor vessel.

However, neither treatment was effective in promoting explosions in the temperature range 830–960° in quartz. On the contrary, the only effect observed from these surface treatments was a moderate elevation of the explosion limit in the low temperature range, $T < 830°$.

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[3] Von Elbe and Lewis, *J. Chem. Phys.*, **10**, 366 (1942).

Acknowledgment.—The authors are indebted to Dr. Bernard Lewis for suggestive discussions preceding and during the course of this work.

Summary

A study of the lower explosion limit of the nitrous oxide–hydrogen system reveals the existence of a minimum in the pressure *versus* temperature curve for mixtures of any fixed compositions. The addition of molecular oxygen poisons the explosive reaction, and this suggests that the minimum is due to the poisoning of the reaction by oxygen from the thermal decomposition of nitrous oxide. In view of the results of Melville's study of the slow reaction, the mechanism of poisoning must be $H + O_2 + M \rightarrow HO_2 + M$.

After passing through the minimum, the explosion limit does not increase indefinitely as the temperature is raised. Above 900° it decreases again in a vycor vessel, but could not be observed to decrease in quartz vessels of the size employed. In vycor above 900°, the explosion is not strongly affected by added oxygen and this insensitivity would be expected from the interpretation of the low temperature results.

ABERDEEN PROVING GROUND, MD.

RECEIVED APRIL 21, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF ETHYL CORPORATION]

Studies in the Lead Chloride–Lead Bromide System[1]

BY GEORGE CALINGAERT, FRANCES W. LAMB AND FRED MEYER

The published information on the lead chloride–lead bromide system is incomplete and contradictory, and after a preliminary examination of its X-ray diffraction characteristics it became obvious that previously reported work would have to be repeated in order to arrive at a reliable description of the system. This paper covers an investigation of this system which, in addition to a thorough X-ray diffraction analysis, includes a repetition and an extension of the work of other investigators by thermal analysis, by conductivity and by aqueous preparations.

In a recently published study of the binary and ternary systems of lead halides, Mlle. Delgery,[2] contrary to the conclusions of previous investigators,[3] reported the existence of several compounds and eutectics. Her first two papers gave the results of thermal analyses on the three binary systems of lead chloride, lead bromide and lead iodide,[2a] and on the ternary system of these lead halides.[2b] These thermal analyses were supported in a third publication[2c] on six series of unsaturated aqueous solutions, each containing two of the four halides. In each series, the composition of the solute was varied from that of one halide to that of the other, while the total concentration was kept constant. All the conductivity–composition curves reported showed broad minima and sharp maxima, which latter were interpreted by the author as indicating the existence in solution of compounds of the corresponding solute compositions. Furthermore, Delgery proposed such measurements as a valuable adjunct to thermal analysis, reporting that peritectic compounds difficult to detect by thermal analysis were readily detected by such conductance measurements.[2c,2d]

For the lead chloride–lead bromide system Delgery's results indicated the existence of a stable compound, $PbClBr$, a peritectic compound, $PbBr_2 \cdot 3PbCl_2$, a eutectic close to $9PbBr_2 \cdot 16PbCl_2$, and several series of solid solutions, two of which had limited miscibility. These results contradicted the earlier thermal analysis of Mönkemeyer,[3a] who found that this system was one in which there was a continuous series of solid solutions with the melting (liquidus) points of all intermediate compositions lying on a straight line joining the melting points of the pure components. The work of Mönkemeyer was directly confirmed by Favorskii,[3b] and indirectly by Matthes[3c] in a study of the ternary system, lead chloride–lead bromide–lead iodide. A comparison of the results obtained by Delgery, Mönkemeyer and Favorskii is given in Fig. 1.

On the other hand, Thomas,[4] in 1898, claimed, like Delgery, to have prepared both $PbBr_2 \cdot 3PbCl_2$ and $PbClBr$. His evidence that $PbBr_2 \cdot 3PbCl_2$ was a compound rather than a solid solution was based on the constancy of the composition of the material crystallizing out of a hot solution of lead chloride to which potassium bromide had been added. His evidence for the existence of $PbClBr$ was even less satisfactory, since his material was obtained only by heating $PbClI$ in a current of bromine.

Experimental

Materials.—Except for lead bromide, these were of analytical reagent quality; all were used without further purification. Spectrographic analysis of the potassium chloride, lead chloride and lead bromide showed a total metallic impurity of less than 0.007, 0.01 and 0.01%, respectively. Chemical analysis of the lead chloride gave

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(1) The X-ray diffraction portion of this study was presented before the Sixth Annual Pittsburgh Conference on X-Ray and Electron Diffraction on November 19, 1948.

(2) (a) Delgery, *Compt. rend.*, **222**, 886 (1946); (b) **223**, 401 (1946); (c) **224**, 274 (1947); (d) **224**, 915 (1947).

(3) (a) Mönkemeyer, *Neues Jahrb. Mineral. Geol.* (Beilage Bd.), **22**, 1 (1906); (b) Favorskii, *Ann. secteur. anal. phys.-chim., Inst. chim. gén.* (*U. S. S. R.*), **13**, 281 (1940); (c) Matthes, *Neues Jahrb. Mineral. Geol.* (Beilage. Bd.), **31**, 342 (1911).

(4) Thomas, *Bull. soc. chem.*, [3] **19**, 598 (1898); [3] **21**, 532 (1899); *Compt. rend.*, **128**, 1234 (1899).