Kinetic Studies of Ammonia Oxidation in Shock Waves. I. The Reaction Mechanism for the Induction Period

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The catalytic oxidation of ammonia has been studied extensively. On the contrary, however, because of the relatively lower reactivity of ammonia, only a few works can be found on non-catalytic oxidation. Stephens and Pease obtained only qualitative results from their flow[1] and static[2] experiments. Volders and Van Tiggelen[3] proposed a mechanism involving NH_2, OH and NOH for the slow thermal reaction. Recently, Husain and Norrish[4] investigated the photolytic oxidation of ammonia by the flash photolysis method and by kinetic spectroscopy. They postulated a mechanism in which a relatively stable intermediate, HNO, plays the role as a degenerate branching reagent, although they themselves could not actually detect it.

However, no information can be found with respect to the mechanism responsible for the high-temperature oxidation of ammonia. In order to clarify this, we have made experiments at temperatures between 1550 and 2300°K by using the shock-tube technique combined with the spectroscopic method. In this paper, we will report on the results obtained from the measurements of the induction periods for the appearance of OH and of the time relations among the concentration changes of NH, NH_2, NO and OH.

Experimental

The experimental arrangements were much the same as have been reported previously:[5] by means of a Shimadzu QR-50 monochromator and an R106 photomultiplier, the ultraviolet absorptions of OH and NH and the intensity distributions of light emitted at various wavelengths were measured.

The reaction mixtures were prepared in an all-glass apparatus with a 10 l. reservoir and were stirred magnetically for an hour before being used. Commercial ammonia (99.98%), oxygen (99.5%) and argon (99.999%) were used without further purification.

Results

Induction Period.—The induction period for the appearance of OH absorption was measured in reflected shock waves for two mixtures at initial pressures from 50 to 110 mmHg. The experimental conditions covered are presented in Table I.

The induction period was found to be dependent neither on the ammonia concentration nor on the product of the ammonia and oxygen concentration, but on the oxygen concentration alone over the 1.5—0.67 range of the ammonia to oxygen ratio, as is shown in Fig.

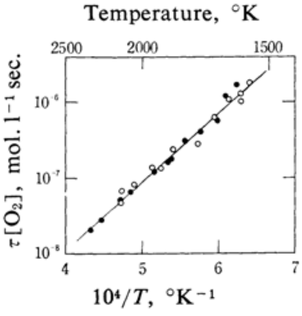

Fig. 1. Induction period for appearance of OH-absorption vs. reciprocal temperature. Open and solid circles are obtained from mixtures I and II (see Table I), respectively.

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[1] E. R. Stephens and R. N. Pease, *J. Am. Chem. Soc.*, **72**, 1188 (1950).

[2] E. R. Stephens and R. N. Pease, ibid., **74**, 3480 (1952).

[3] A. Volders and A. Van Tiggelen, *Bull. soc. chim. Belg.*, **63**, 542 (1954).

[4] D. Husain and R. G. W. Norrish, *Proc. Roy. Soc.*, **A 273**, 245 (1963).

[5] T. Takeyama and H. Miyama, This Bulletin, **38**, 936, (1965).

TABLE I. EXPERIMENTAL CONDITIONS

Mixture	$\%O_2$	$\%NH_3$	%Ar	Temp. range °K	Press. range atm.	$[O_2]$ range 10^{-3} mol./l.
I	6	4	90	1550—2110	3.5—5.5	1.23—2.47
II	4	6	90	1600—2300	3.5—4.5	0.741—1.37

1. The least-squares line in the figure is expressed by:

$$\log \tau [O_2] \ (\text{mol. l}^{-1}\text{sec.}) = -11.71 + (9300 \pm 270)/T$$

where the temperature dependence corresponds to an activation energy of 42.5±1.2 kcal./mol.

The pressure of the reaction system was measured simultaneously at the same location in the tube by a quartz transducer. However, the pressure increase due to the reaction was far less than that found by us in the oxidation of hydrogen,[6] acetylene[5] and methane[7]; it was not appreciable in most runs.

The Spectroscopic Identification of Reaction Intermediates.—The reaction intermediates, the NH radical, nitric oxide and the NH_2 radical, were identified by measuring the intensity distribution of light emitted in the ultraviolet and visible region:

The NH Radical.—Since NH has a strong band emission at 3360 Å due to its $^3\Pi \rightarrow {}^3\Sigma$ transition,[8] the intensities of light emitted at 1960±10°K were measured over the 3270—3430 Å wavelength range. The width of the exit slit of the monochromator was set at 0.20 mm., allowing a band pass of about 12Å. The results are shown in Fig. 2, where the intensities given in the ordinate are corrected with the spectral response of the R106 photomultiplier and divided by the intensities, which were measured simultaneously by means of an interference filter (Baird-Atomic, Inc., λ_{max}: 3070Å, transmission at λ_{max}: 13%, half width: 120Å) and an RCA 1P28 photomultiplier. There is a sharp peak at 3360 Å; hence, the existence of the NH radical is definite.

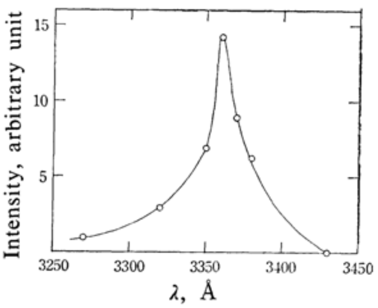

Fig. 2. Intensity distribution of light emitted between 3250 and 3450Å.
Mixture II, initial pressure 55.0 mmHg, shock temperature 1960±10°K

Nitric Oxide.—The β-band of nitric oxide has weak emissions at 4303 and 4310Å because of its $B^2\Pi \rightarrow X^2\Pi$ transition.[9] Therefore, the intensity distribution was measured over the 4215—4360Å wavelength range, with the slit width of the monochromator being set at 0.25 mm. and the band pass at 30Å. The results obtained at 2120±30°K are shown in Fig. 3, where the intensities are treated as has been described above. Although the peak near 4300Å is less definite than that found at 3360 Å, it may be attributed to nitric oxide, for there is no other possible emitter at this wavelength.

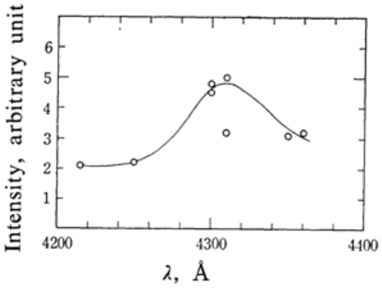

Fig. 3. Intensity distribution of light emitted between 4200 and 4400Å.
Mixture I, initial pressure 50.0 mmHg, shock temperature 2120±30°K

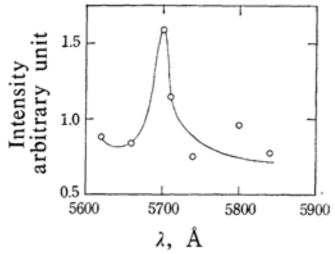

Fig. 4. Intensity distribution of light emitted between 5600 and 5900Å.
Mixture II, initial pressure 55.0 mmHg, shock temperature 1970±20°K

The NH_2 Radical.—The visible emission of NH_2, which is found in oxy-ammonia flames

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[6] H. Miyama and T. Takeyama, *J. Chem. Phys.*, **41**, 2287 (1964).

[7] H. Miyama and T. Takeyama, ibid., **40**, 2049 (1964); This Bulletin, **38**, 37 (1965).

[8] A. G. Gaydon, "The Spectroscopy of Flames," Chapman & Hall Ltd., London (1957), p. 242.

[9] R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," Chapman & Hall Ltd., London (1950), p. 180.

and is called the ammonia α-band, is composed of a very large number of fine lines as a result of its rotational structure.[10] We have tried to find the bright band at about 5705 Å,[10] measuring the intensities of light emitted at 1970±20°K over the 5620—5840 Å wavelength range; the slit width of the monochromator was set at 0.1 mm., which allows a band pass of 30 Å. As is shown in Fig. 4, a peak is observed at 5700 Å, thus confirming the existence of NH_2 radicals.

Concentration Changes of Intermediate Species with Time.—In order to observe the concentration changes of the above-described intermediates in the course of the reaction, the changes in the absorption and/or the emission of these species were followed by means of a monochromator with a photomultiplier. Since, however, the experimental arrangement does not allow the simultaneous measurements of absorptions or emissions of all these species, the ultraviolet emission, which was measured simultaneously at the auxiliary observation station by a Baird-Atomic interference filter and an RCA 1P28 photomultiplier, has been used as a reference standard for the time scale. A typical example of the changes observed in this way can be seen in Fig. 5, which was obtained by shock-heating the reaction mixture II at an initial pressure of 65.0 mmHg to 1840 ±10°K.

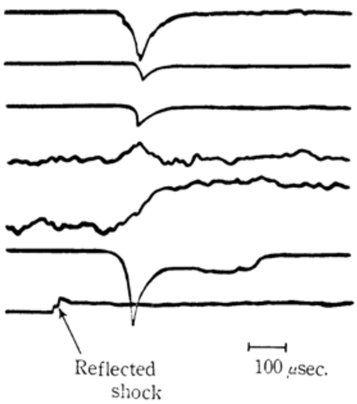

Fig. 5. Changes in absorption and/or emission of various intermediates with time. Traces represent, from top to bottom, NH_2-, NO- and NH-emission, NH- and OH-absorption, the ultraviolet emission measured by an interference filter, and pressure.
Mixture II, initial pressure 65.0 mmHg, shock temperature 1840±10°K

The general features observed under various conditions are as follows: (a) the absorptions of OH and NH appear at the same time, after the arrival of the reflected shock; (b) the emissions of NH and nitric oxide appear and reach their maxima at almost the same time, while the emission of NH_2 seems to reach its maximum a little earlier than do those of NH and nitric oxide; and (c) the absorption of NH reaches its maximum earlier than that of OH and decays within a few tens of micro seconds.

Discussion

The experimental observations a and b, concerning the time relations of various intermediates, lead us to postulate the following reaction scheme as the main steps governing the induction period of the high-temperature, homogeneous oxidation of ammonia:

$$NH_2+O_2 \rightarrow NH+HO_2 \qquad (I)$$

$$NH+O_2 \rightarrow NO+OH \qquad (II)$$

$$OH+NH_3 \rightarrow NH_2+H_2O \qquad (III)$$

The HO_2 radical produced in Reaction I is unstable at these high temperatures[6] and so may soon decompose into OH and O by Reaction IV rather than reacting with ammonia.

$$HO_2 \rightarrow OH+O \qquad (IV)$$

The oxygen atom will then abstract hydrogen from ammonia by Reaction V; the reactions between such intermediates as NH_2, NH, OH and O should be excluded from the reaction scheme for the induction period.[6,7]

$$O+NH_3 \rightarrow OH+NH_2 \qquad (V)$$

An application of the treatment given by Schott and Kinsey for the hydrogen-oxygen reaction[11] to Reactions I—V will explain the dependence of the induction period on the oxygen concentration and the activation energy obtained from the temperature coefficient. By assuming that the principal chain carrier is the NH_2 radical, and that the OH, O, NH and HO_2 radicals are steady-state intermediates, [OH] and the rate of formation of the NH_2 radical are expressed by Eqs. 1 and 2 respectively:

$$[OH]=3k_1[O_2][NH_2]/k_3[NH_3] \qquad (1)$$

$$d[NH_2]/dt=3k_1[O_2][NH_2] \qquad (2)$$

Here, k_1 and k_3 are the rate constants of Reactions I and III respectively.

The integrated form of Eq. 2, assuming that the concentrations of ammonia and oxygen are not decreased during the induction period, is:

$$[NH_2]=[NH_2]_0\exp\{3k_1[O_2](t-t_0)\} \qquad (3)$$

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[10] Ref. 9, p. 178.

[11] G. L. Schott and J. L. Kinsey, *J. Chem. Phys.*, **29**, 1177 (1958).

where t_0 is any reference time following which Eqs. 2 and 3 are valid, and the concentration with the subscript zero represents the concentration at $t=t_0$. It is assumed that at $t_0=0$ the rate of the chain branching becomes equal to the rate of initiation, although the initiation step can not be identified in the present study. [OH] can then be expressed by Eq. 4 and builds up exponentially, as has been found experimentally:

$$[\mathrm{OH}] = [\mathrm{OH}]_0 \exp(3k_1[\mathrm{O_2}]t) \qquad (4)$$

$[\mathrm{OH}]_0$ is given by Eq. 1.

Therefore,

$$\log\{[\mathrm{OH}]_\tau/[\mathrm{OH}]_0\} = 1.303\, k_1[\mathrm{O_2}]\tau \qquad (5)$$

$[\mathrm{OH}]_\tau$ being the concentration at the end of the induction period.

If it can be assumed, as in the hydrogen-oxygen reaction,[11] that the $[\mathrm{OH}]_\tau/[\mathrm{OH}]_0$ ratio remains approximately constant over the temperature range studied, the following relation is obtained from Eq. 5:

$$\tau[\mathrm{O_2}] \propto 1/k_1 \qquad (6)$$

Therefore, a plot of $\log(\tau[\mathrm{O_2}])$ against $1/T$ would give a straight line, the slope of which corresponds to the activation energy of Reaction I. This has been found to be true, as has been described in the preceding section; the straight line shown in Fig. 1 gives an experimental activaion energy of 42.5 ± 1.2 kcal./mol. for Reaction I, which is endothermic by 41 kcal./mol., if the bond energies of NH–H and $\mathrm{H{-}O_2}$ are taken to be, respectively, 88[12,16] and 47[16] kcal./mol. The relatively small difference between the activation energy and the endothermicity may be due to the low activation barrier which is usually found in free radical reactions.[17] The results from the induction period measurements, therefore, suggest strongly that Reaction I is rate-controlling.

In the photolytic oxidation of ammonia, Husain and Norrish[4] have found NH, OH and nitric oxide to be absent in the initial stages of the reaction and have, therefore, postulated the following scheme:

$$\mathrm{NH_2+O_2 \rightarrow HNO+OH} \qquad (\mathrm{VI})$$

$$\mathrm{OH+NH_3 \rightarrow NH_2+H_2O} \qquad (\mathrm{VII})$$

$$\mathrm{HNO \rightarrow H+NO} \qquad (\mathrm{VIII})$$

$$\mathrm{2HNO \rightarrow H_2O+N_2O} \qquad (\mathrm{IX})$$

where they regarded the HNO intermediate as a degenerate branching reagent, although they could not detect it. At high temperatures such as those studied by us, the HNO molecule cannot be stable enough to play such a role. Furthermore, it is impossible for their scheme VI—IX to account for the experimental activation energy of 42.5 kcal./mol. and for Findings a and b.

Volders and Van Tiggelen[3] studied, by the static method, the slow oxidation of ammonia around 800°K and proposed the following mechanism:

$$\mathrm{NH_3 \xrightarrow{wall} NH} \qquad (\mathrm{X})$$

$$\mathrm{NH+O_2 \rightarrow NO+OH} \qquad (\mathrm{XI})$$

$$\mathrm{OH+NH_3 \rightarrow NH_2+H_2O} \qquad (\mathrm{XII})$$

$$\mathrm{NH_2+O_2 \rightarrow NOH+OH} \qquad (\mathrm{XIII})$$

$$\mathrm{OH+NO \rightarrow HNO_2} \qquad (\mathrm{XIV})$$

Since NOH was not detected, Reaction XIII is rather speculative and open to question. In addition, the heterogeneous Reaction X yielding NH should be ruled out for the reaction in shock waves.

Therefore, our mechanism accounts most reasonably for the experimental findings concerning the induction period, i. e., for those except Finding c. In order to explain this, it is necessary to obtain the reaction profile after the induction period by using the values of rate constants, the concentrations of intermediates, and their thermochemical properties. Unfortunately, the available data at present are inadequate for carrying out such a numerical calculation.

Summary

The oxidation of ammonia has been studied at temperatures between 1550 and 2300°K by using the shock-tube technique combined with ultraviolet absorption spectroscopy.

The measurements of the induction periods for the appearance of OH have shown that they are strongly dependent on the concentration of oxygen and that the activation energy required is 42.5 ± 1.2 kcal./mol.

The intermediates of the reaction, NH, NO and $\mathrm{NH_2}$, have been detected spectroscopically, and the time relations between their appearance and their accumulation have been determined.

As a result, the following mechanism has been postulated as the main steps governing the induction period of the high-temperature oxidation of ammonia:

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[12] E. D. Coon, *Proc. N. Dakota Acad. Sci.*, 7, 46 (1953); This value is also calculated from the values of the bond energies of $\mathrm{NH_2}$-H and N-H and of the average N-H bond energy in ammonia, if they are taken to be 106,[13] 85[14] and 93[15] kcal./mol., respectively.

[13] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 29, 442 (1958).

[14] A. G. Gaydon "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London (1953), p. 228.

[15] Ref. 14, p. 170.

[16] A. P. Altshuler, *J. Chem. Phys.*, 22, 1947 (1954).

[17] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. I, Princeton University Press (1958), p. 4.

$$NH_2 + O_2 \rightarrow NH + HO_2 \qquad (I)$$

$$NH + O_2 \rightarrow NO + OH \qquad (II)$$

$$OH + NH_3 \rightarrow NH_2 + H_2O \qquad (III)$$

$$HO_2 \rightarrow OH + O \qquad (IV)$$

$$O + NH_3 \rightarrow OH + NH_2 \qquad (V)$$

where Reaction I is considered to be rate-controlling.

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