[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics of the Non-catalytic Oxidation of Ammonia: Flow Experiments[1]

BY EDGAR R. STEPHENS AND ROBERT N. PEASE

Although the oxidation of ammonia in presence of platinum gauze and other catalysts has been widely studied, little attention has been paid to the non-catalytic reaction. This reaction apparently occurs with some difficulty since a small jet of ammonia in air will not support a stable flame even though the calculated heat of combustion to nitrogen and water is 75,700 cal. per mole of ammonia. Further a stoichiometric ammonia–air mixture at room temperature and pressure is not ignited by a spark from a small induction coil, though White[2] was able to initiate upward (but not downward) propagation in a 5-cm. tube by exploding 1–2 mg. of guncotton yarn in the mixture. Substitution of oxygen for air considerably increases ignitibility (the mixtures will even detonate) but ammonia is still not a very satisfactory substitute for hydrogen or natural gas in a blast lamp, as direct trials have shown. It was this rather marked inertness of ammonia in combustion processes which led to the experimental work to be reported.

Experimental Method

Exploratory experiments were instituted using the flow method at atmospheric pressure. Ammonia and oxygen were introduced directly from tanks through capillary flow meters.[3] They were mixed in a short length of tubing joined to the reaction tube inside the furnace. The reaction tube itself was of quartz, about 2-cm. diameter and 15-cm. long with a volume of 41 cc. A second tube was also constructed, and was filled with lengths of quartz tubing to increase the surface about five fold. Its free volume was 28.3 cc. The standard total flow rate was 40 cc. per min. at 25° and 1 atm. for the unpacked tube. This was reduced to 28 cc./min. for the packed tube to compensate for the smaller volume. These reaction tubes were later coated with potassium chloride.

The extent of reaction was determined by absorbing the ammonia in a stream of standard hydrochloric acid solution which dripped slowly from a buret into an absorbing tower packed with broken glass through which the effluent gas flowed. Excess of acid was then titrated with standard alkali. Constant checks on the make-up mixture were obtained by by-passing the reaction tube from time to time.

Temperature Measurement and Control.—The temperature in the furnace was measured using a three junction chromel–alumel thermocouple with a potentiometer. When used with the cold junctions at 0° this gave a potential of 90.4 millivolts at 725°. The temperature was automatically controlled by means of a saturable reactor-type controller which was in series with one branch of the furnace windings. The impedance which the controller presents to the furnace current was controlled by the unbalanced current from an a. c. wheatstone bridge, one leg of which was a platinum resistance thermometer placed inside the furnace. With a reasonably steady voltage supply this circuit will control the temperature to within one or two degrees.

Results and Discussion

Preliminary measurements were attempted with a 50% mixture at 600° in a Pyrex reaction tube. Since conversions were very small and erratic, the quartz tube was shortly installed and the temperature was raised. It then began to appear that as the per cent. ammonia was *diminished*, conversions *rose* rather sharply. Thus for a 6.25% ammonia mixture at 600° the conversion was nearly complete, whereas it had only amounted to 1–2% for a 50% mixture. Further tests proved that the temperature could be dropped 200° (to 400°) before the percentage conversion of the 6.25% mixture became equivalent to that of the 50% mixture at 600° (see Table I, tube A). An essential peculiarity of the ammonia oxidation thus emerged at once—apparently ammonia inhibits its own reaction with oxygen.[4] This may very well account for the poor combustion characteristics.

The result recalls an interesting observation made by Taylor and Salley on the ammonia-sensitized photochemical hydrogen–oxygen combination.[5] With 400 mm. hydrogen and 200 mm. oxygen, the rate passed through a sharp maximum at 5–10 mm. ammonia (290–405°). It is apparent that chain initiation by photochemical action is effective at lower pressures whereas, ". . . at concentrations greater than the optimum, a chain breaking effect of ammonia is predominant." An analogous conclusion follows for the thermal oxidation of ammonia itself.

Additional experiments were carried out to determine the effect of surface on the thermal reaction. For this purpose a quartz tube was filled with lengths of quartz tubing to give about a fivefold increase in surface. It was found that in general the conversions were not greatly affected (Table I—compare tube B with tube A). Both the empty and the packed tubes were then treated with potassium chloride by rinsing with a 10% potassium chloride solution, draining and drying. This treatment has been found to diminish the rate of oxidation of a number of substances.[6] Ammonia proved to be no exception. For example, the conversion of a 6.25% mixture at 600° was reduced from 97 to 9.8%. However, at higher concentrations and temperatures the effect was less marked. (Compare tubes C and D with A and B, Table I.) Again the rates in empty and packed tubes (after coating) were not greatly different.

These results present something of a paradox. On the one hand, the equality of conversions in empty and packed tubes indicates independence of surface. On the other hand, the depressant action of the potassium chloride coating points to surface activity. Analogous results have been obtained in the thermal hydrogen–chlorine reaction.[7] They may be rationalized by assuming that chains both start and stop at the walls. However, the self-

---

(1) The work described in this paper was done in connection with Contract NOrd 7920 with the U. S. Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, Project Bumblebee, and with Contract N6-ori-105 with the Office of Naval Research, U. S. Navy, as coördinated by Princeton University, Project Squid. Acknowledgment is due Dean H. S. Taylor, who has general supervision of this work.

(2) White, *J. Chem. Soc.* (*London*), **121**, 1688 (1922), contains references to earlier work.

(3) Mineral oil was used in the ammonia flow meter and constant-head overflow.

(4) Of course the oxygen concentration rose as that of ammonia fell. Nevertheless the change is not great—from 0.50 to 0.94 atm.—whereas the rate rose by a factor of at least 50 at 600°.

(5) Taylor and Salley, THIS JOURNAL, **55**, 96 (1933).

(6) Pease and Chesebro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928), and later papers.

(7) Pease, THIS JOURNAL, **56**, 2388 (1934); Morris and Pease, *ibid.*, **61**, 391 (1939).

TABLE I

PER CENT. OF AMMONIA REACTED IN AMMONIA–OXYGEN MIXTURES

% NH_3 in Uncoated tubes	Reaction[a] tube	Temp. 400°	450°	500°	525°	550°	600°	625°	675°	725°
		Per cent. ammonia reacted								
1	A	2	8	67	91	100	(100)	...	...	....
	B	...	...	..	..	...	100	...	...	....
6.25	A	1.5	3.0	10.3	..	48.5	99.5	...	...	(100)
	B	...	...	..	..	...	97	...	...	....
12.5	A	...	1.5	2.5	8.2	20.4	71.4	100	...	(100)
	B	...	4.3	4.4	..	21.1	81.1	100	...	....
18.75	A	...	...	..	..	10.7	40.0	...	...	....
	B	...	...	..	..	...	53.9	...	...	....
25.0	A	...	...	..	..	...	30.2	...	...	100
	B	...	...	..	..	...	37.4	...	...	....
31.25	A	...	...	..	..	...	18.3	...	...	....
	B	...	...	..	..	...	18.6	...	...	....
37.5	A	...	...	..	..	...	10.3	...	...	....
	B	...	...	..	..	...	11.6	...	...	....
43.75	A	...	...	..	..	...	5.6	...	...	....
	B	...	...	..	..	...	9.1	...	...	....
50.0	A	...	...	..	..	...	(1–2)	...	4.0	12.5
	B	...	...	..	..	...	....	...	6	13
75.0	A	...	...	..	..	...	....	...	...	5
	B	...	...	..	..	...	....	...	...	4.1
Coated tubes										
1	D	...	...	..	..	...	11.9	...	...	....
6.25	C	...	...	..	..	1.3	....	...	...	100
	D	...	...	..	..	...	9.8	...	...	....
12.5	C	...	...	..	..	0.8	0.6	...	...	13.1
	D	...	...	..	..	3.2	1.8	2.9	...	....
18.75	D	...	...	..	..	...	1.5	...	...	....
25.0	D	...	...	..	..	...	1.1	...	...	....
31.25	D	...	...	..	..	...	0	...	...	....
50.0	C	...	...	..	..	...	....	...	...	10.2
	D	...	...	..	..	...	....	...	1.2	4.7
75.0	D	...	...	..	..	...	....	...	...	3.0

[a] Reaction tubes: A, empty, uncoated; B, packed, uncoated; C, empty, coated; D, packed, coated. Tubes A and C, 41-cc. volume; flow rate 40 cc. per min. at 25° and 1 atm.; tubes B and D, 28.3-cc. volume; flow rate 28 cc. per min.

inhibition by ammonia would then demand that this is also associated with the wall process. Whether these qualitative conclusions can be justified remains to be seen.

Though the data are unsuited to a determination of the kinetics of the process, there is one indication which may be of interest. It has been mentioned that the per cent. ammonia reacting rises rapidly as the ammonia content of the initial mixture decreases. It turns out that over a part of the range, the product of concentration and per cent. reacted (*i. e.*, the amount of ammonia reacted) is roughly constant. True constancy would have indicated a zero-order reaction with respect to ammonia

$$-\frac{dp}{dt} = k;\ k = \frac{p_0 - p}{t} = \frac{p_0 x}{t}$$

where p_0 = initial pressure of ammonia, and x = fraction converted. Values of the "constant" have been calculated from the percentage conversions for the runs in tube A (empty, uncoated) at 600°. The value of t is taken as

$$\frac{41}{40} \times \frac{298}{873} \times 60 = 21 \text{ sec.}$$

the flow rate at 25° and 1 atm. being 40 cc. per min. and the tube volume being 41 cc. Two values obtained at a flow rate of 252.5 cc. per minute are added, the corresponding reaction time being taken as 3.3 sec. Results are given in Table II. It will be seen that even this constant falls as the ammonia concentration rises much above 25%—that is to say, the rate then varies inversely as the ammonia concentration. No special significance is attached to these calculations except as they illustrate the unusual dependence on ammonia concentration.

The data of Table I may also be used to obtain an apparent activation energy from the temperature coefficient. Values of the corresponding k_0 are given in Table III. Plots of log k_0 *vs.* $1/T$ do not give good straight lines, but it may be concluded that the apparent activation energy is of the order of 30,000 cal. per mole. This is quite low considering the temperature range in which the measurements were made.

TABLE II

VALUES OF ZERO-ORDER CONSTANT WITH RESPECT TO AMMONIA AT 600°

p_0NH_3 atm.	Fract. convers. x	k_0 atm./sec. $\times 10^3$
Tube A, empty, uncoated; t = 21 sec. (40 cc. per min. total flow)		
0.0625	0.995	(3.0)
.125	.714	4.3
.1875	.400	3.6
.250	.302	3.6
.3125	.183	2.8
.375	.103	1.8
.4375	.056	1.1
t = 3.3 sec.		
0.0625	0.373	6.9
.125	.125	4.3
Tube B, packed, uncoated, t = 21 sec.		
0.0625	0.97	(2.9)
.125	.811	4.9
.1875	.539	4.9
.250	.374	4.5
.3125	.186	2.8
.375	.116	2.1
.4375	.091	1.9

The question of isoluble intermediates was investigated with little success. Nitrite and nitrate ions could not be detected in the solution after absorption of ammonia. There was occasional evidence of nitrogen oxides (a very faint odor) but only in very low concentration. It was also found that under certain conditions starch–iodide test paper was colored slowly by the product gases, and that acidified permanganate was bleached, indicating a trace of peroxide. It is concluded that the products are very largely nitrogen and water.

TABLE III

EFFECT OF TEMPERATURE

Flow rate, 40 cc. per min. at 25° and 1 atm.; Tube A, empty, uncoated; 41 cc. volume

Temp., °C.	Fract. conv., x	t sec.	k_0 $\times 10^5$
Initial comp., 6.25% NH_3			
400	0.015	27.3	3.4
450	.030	25.4	7.4
500	.103	23.7	27
550	.485	22.3	136
600	.995	21.0	296
Initial comp., 12.5% NH_3			
450	0.015	25.4	7.4
500	.025	23.7	13
525	.082	23.0	45
550	.204	22.3	114
600	.714	21.0	425

Further experiments by the static method are under way. Measurements of pressure change are planned, though this is not too satisfactory since the change in number of moles on complete reaction is only from 3.5 to 4. Such measurements will be supplemented by analysis.

Summary

The slow non-catalytic reaction between ammonia and oxygen has been studied by the flow method. It has been found that the fraction reacted increases rapidly as the ammonia concentration is decreased, indicating a zero (or negative) order. Thus ammonia appears to inhibit its own oxidation. Rates in empty and packed reaction tubes are about the same; but coating with potassium chloride causes a marked decrease in both cases.

PRINCETON, N. J. RECEIVED AUGUST 3, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Promoter Effect of Platinic Chloride on Raney Nickel. I. General Effects on Type W-6 Catalyst

BY DEWEY ROBERT LEVERING, FRED L. MORRITZ AND EUGENE LIEBER

In 1936, Lieber and Smith[1a] found that small amounts of platinic chloride, added to Raney nickel catalyst just prior to the start of the reduction, produced a marked enhancing effect on the activity of the catalyst for a variety of functional groups. It was clearly demonstrated that the promoting effect obtained was markedly beyond that which could be expected on the basis of the quantity of platinum metal used. Further studies[1b,1c] on the platinum chloride promotion dealt with the hydrogenation of nitrocompounds at one atmosphere pressure.

Since this early investigation there has been a marked enhancement in the activity of the Raney nickel catalyst itself due to improvements in the procedure for the preparation of the catalyst from the Raney alloy[2a] over that of the method[2b] used in the early investigation.[1a] Accordingly, it was considered important to investigate the promoter effect on the improved types of Raney nickel now available, particularly that designated

---

[1] (a) E. Lieber and G. B. L. Smith, THIS JOURNAL, **58**, 1417 (1936); (b) J. R. Reasenberg, E. Lieber and G. B. L. Smith, *ibid.*, **61**, 384 (1939); (c) S. S. Scholnik, J. R. Reasenberg, E. Lieber and G. B. L. Smith, *ibid.*, **63**, 1192 (1941).

[2] (a) H. Adkins and H. R. Billica, *ibid.*, **70**, 695 (1948); (b) H. Adkins and L. W. Covert, *ibid.*, **54**, 4116 (1932).