[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics of the Non-Catalytic Oxidation of Ammonia: Static Experiments in an Empty Uncoated Silica Vessel[1]

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A study of the oxidation of ammonia in an uncoated silica reaction vessel indicates that the rate increases in passing from ammonia-rich to -lean mixtures. On the rich side, rates are roughly proportional to the product of ammonia and oxygen concentrations, whereas on the lean side the square of the oxygen concentration seems to be involved. The activation energy approximates 45,000 cal. in both regions.

In a previous paper[2] the results of an investigation of the oxidation of ammonia carried out in a flow system were reported. Two rather striking features of this reaction became evident in the course of this investigation. First, the percentage of ammonia oxidized rose rather sharply as the percentage ammonia in the mixture was decreased. Data were presented which indicated that at low ammonia concentrations the rate was approximately zero order in ammonia. At higher ammonia concentrations the zero order rate constant decreased, indicating either an inverse dependence of rate on ammonia concentration or a direct dependence on oxygen concentration. The second feature of this reaction which was discovered in the original flow studies was the striking role played by the surface of the reaction vessel. Briefly, the approximate equality of conversions in empty and packed quartz reaction tubes indicated that the reaction was independent of the surface. On the other hand, a coating of potassium chloride on either the empty or the packed reaction tube was found to suppress the reaction very markedly, indicating that surface does play a role. These facts were partially reconciled by assuming that reaction chains both start and stop on the walls. Since the data obtained in the flow system were not suited to a study of the kinetics of the reaction, further experiments were undertaken in a static system.

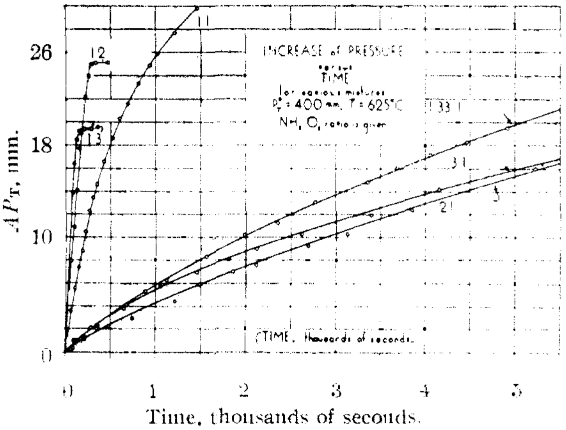

Fig. 1.—Increase of pressure *versus* time for various mixtures: $P_T{}^0$ = 400 mm., T = 625°; $NH_3:O_2$ ratio is given.

Experimental Method

The apparatus used was of conventional design. The reaction bulb was constructed of fused quartz in order to operate at temperatures up to 725°. The bulb was cleaned by washing with water. Ammonia and oxygen were introduced in the desired proportion, and at the proper total pressure, directly into a mixing chamber without purification. Opening a stopcock allowed this mixture to enter the previously evacuated reaction vessel through a combination mercury manometer and cut-off. The mercury was then raised to a reference mark to isolate the reaction vessel and the pressure at constant volume followed as a function of time. The initial partial pressures of the two gases were obtained from the ratio of their partial pressures in the mixing chamber and the initial total pressure in the reaction bulb. This latter could be obtained either from the pressure in the mixing chamber after pressure equilibration with the reaction bulb or by extrapolation of the pressure–time curve. The temperature of the furnace which contained the reaction bulb was measured and controlled by the system employed in the previous work.[2] Since pressure was being used as a measure of extent of reaction and the initial slopes of the pressure *versus* time curves were of interest, it was imperative that the temperature be controlled quite accurately, especially in view of the fact that only a small pressure change accompanies this reaction. It was necessary to keep the capillary lead between the reaction bulb and the mercury manometer warm by means of an electrical heater to prevent condensation of the water formed in the oxidation reaction.

Results and Discussion

Typical pressure–time plots for ammonia–oxygen mixtures at 400 mm. total initial pressure and a temperature of 625° in a water-washed silica reaction vessel are presented in Fig. 1. The curves separate rather sharply into two groups, rates being relatively low for the stoichiometric mixture (1.33 NH_3: 1 O_2) or those with ammonia in excess, and relatively high with deficient ammonia. This is the type of behavior already noted in the flow experiments at 1 atm.[2] The magnitude of the difference is considerable; comparison of the 1:3 and 3:1 mixtures gives a ratio of rates of about 30 to 1.

Such a wide spread rules out any simple dependence on concentration. An equation like

$$\frac{dP}{dt} = k\frac{[O_2]^2}{1 + [NH_3]/[O_2]}$$

accounts roughly for the over-all variation; however there is some evidence that the concentration dependence is different in the two regions.

As a basis for further analysis, data on a series of

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[2] E. R. Stephens and R. N. Pease, THIS JOURNAL, **72**, 1188 (1950).

runs at 200, 300 and 400 mm. initial pressure are presented in Table I for each of six mixture compositions. Values of initial rates, times to 25% reaction, and times to 50% reaction are given. As is so often true of oxidation reactions, reproducibility and consistency are not of a high order. In addition, pressure increases are relatively small (one-fourth of the ammonia, or one-third of the oxygen—whichever is deficient) and run uniformly only 75 to 80% of the expected final value for nitrogen and water vapor as products. As a consequence any conclusions must be somewhat provisional.

In spite of the variability of the data, certain conclusions emerge fairly clearly from Table I. Thus there is the sharp change in rate as the NH_3/O_2 ratio is decreased, already noted in Fig. 1. That this should occur over so small a range of mixture ratio as that represented by 4:3 and 1:1 mixtures admittedly is difficult to accept but the data are consistent on this feature. Apparently there is an abrupt change in kinetics as the stoichiometric ratio is passed.

TABLE I

EFFECT OF PRESSURE ON RATE FOR VARIOUS AMMONIA–OXYGEN MIXTURES AT 625°

P_0,[a] mm.	$[\mathrm{d}P/\mathrm{d}t]_0$ $\times 10^3$, mm./sec.	t_{25},[a] sec.	t_{50},[a] sec.	$\frac{1}{P_0}\left[\frac{\mathrm{d}P}{\mathrm{d}t}\right]_0$ $\times 10^8$	P_0t_{25} $\times 10^{-5}$	P_0t_{50} $\times 10^{-5}$
			$3NH_3/1O_2$			
200	1.8	3700	12000	4.5	7.4	24
300	2.0	3300	8700	2.2	9.9	26
400	6.9	1880	5450	4.3	7.5	22
			$2NH_3/1O_2$			
200	2.3	7500	20000	5.8	15	40
300	4.8	4400	13000	5.3	13	39
	5.2	3850	11000	5.8	11.5	33
400	6.8	3400	8800	4.2	13.5	35
			$4NH_3/3O_2$			
200	2.6	7900	25700	6.5	16	51
300	4.7	4900	14300	5.2	15	43
400	8.5	3180	10400	5.3	13	42
			$1NH_3/1O_2$			
200	16	630	2000	40	1.3	4.0
300	27	490	(4750)	30	1.5	(14)
	38	340	1090	42	1.0	3.3
400	71	290	980	44	1.2	3.9
	49	290	940	31	1.2	3.8
			$1NH_3/2O_2$			
200	35	130	270	88	0.3	0.5
300	75	90	190	83	0.3	0.6
400	140	65	140	87	0.3	0.6
			$1NH_3/3O_2$			
200	50	65	130	125	0.1	0.3
300	110	45	95	120	0.1	0.3
400	200	35	70	125	0.1	0.3

[a] Actual pressures are with a few mm. of values given. t_{25} and t_{50} are observed values for $^1/_4$ or $^1/_2$ of the theoretical pressure rise.

Information about kinetics in the two regimes is afforded by analysis of the effect of total pressure for the various mixture ratios. If total pressure appears as a squared term

$$\mathrm{d}P/\mathrm{d}t = kP^2f(x_{NH_3}, x_{O_2})$$

where X_{NH_3} and X_{O_2} are mole fractions, the products $\frac{1}{P_0^2}\left[\frac{\mathrm{d}P}{\mathrm{d}t}\right]_0$, P_0t_{25}, and P_0t_{50} should be constant for a given NH_3/O_2 ratio. A glance at the last three columns of Table I will reveal that this is a reasonably good conclusion.

With respect to the data on initial rates, the following comments are pertinent. For a second-order process

$$\frac{1}{P_0^2}\left[\frac{\mathrm{d}P}{\mathrm{d}t}\right]_0 = kX_{NH_3}X_{O_2}$$

where X_{NH_3} and X_{O_2} are mole fractions in the initial mixture. The products of the latter for 3:1, 2:1 and 4:3 mixtures stand as 1:1.2:1.3. This is roughly the range observed for these three rich mixtures. If the relation is

$$\frac{1}{P_0^2}\left[\frac{\mathrm{d}P}{\mathrm{d}t}\right]_0 = k\,\frac{X^2_{O_2}}{1 + X_{NH_3}/X_{O_2}}$$

the values for 1:1, 1:2 and 1:3 mixtures would be as 1:2.4:3.4. This again approximates the values observed for the lean mixtures. Incidentally the agreement is not as good if the denominator is omitted. Comparison with $X^2_{O_2}$ only gives ratios of 1:1.8:2.3, which is a poorer representation of the data.

With respect to the data on t_{25} and t_{50}, it may be noted that for a second-order process

$$\mathrm{d}P/\mathrm{d}t = kP_{NH_3} \times P_{O_2} = k[(X_{NH_3} + 4)P_0 - 4P]\,[(X_{O_2} + 3)P_0 - 3P]$$

where X_{NH_3}, X_{O_2} and P_0 refer to initial conditions. If the initial ratio is stoichiometric ($4NH_3:3O_2$), this becomes

$$\mathrm{d}P/\mathrm{d}t = 12k[8/7P_0 - P]^2$$

With deficient oxygen (or a stoichiometric mixture)

$$(P - P_0)_{\text{final}} = \frac{1}{3}P_{0_{O_2}} = \frac{1}{3}X_{O_2}P_0$$

For 50% reaction

$$(P - P_0)_{50} = \frac{1}{6}X_{O_2}P_0$$

for 3:1 and 2:1 mixtures, and for the stoichiometric mixture

$$(P - P_0)_{50} = \frac{1}{14}P_0$$

Integrating and solving for P_0t_{50} gives values in the ratio 1:1.22:1.65 for 3:1, 2:1 and 4:3 mixtures. Observed values increase in about this way, though more rapidly. A similar result is obtained for t_{25}.

If the relation for lean mixtures is

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k\,\frac{[O_2]^2}{1 + [(NH_3]/[O_2]}$$

a much more complicated situation is faced unless the mixture ratio in the denominator is identified with the initial ratio. Setting

$$[O_2] = P_{O_2} = [(X_{O_2} + 3)P_0 - 3P] = [B - 3P]$$

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k\,\frac{[B - 3P]^2}{1 + [X_{NH_3}/X_{O_2}]_0}$$

With ammonia now deficient

$$(P - P_0)_{final} = \frac{1}{4}X_{NH_3}P_0$$

$$(P - P_0)_{50} = \frac{1}{8}X_{NH_3}P_0$$

Integrating and solving for P_0t_{50}, the values for 1:3, 1:2 and 1:1 mixture ratios stand as 1:2.0:9.4. The P_0t_{50} product thus should change much more rapidly with mixture ratio. The experimental data are again in reasonable agreement.

The temperature coefficient has been determined for the $2NH_3:1O_2$, and for $1NH_3:2O_2$ mixtures (Table II). Suitable plots give reasonably good straight lines from which activation energies have been calculated. Results vary somewhat but indicate a value in the neighborhood of 45,000 cal., for both rich and lean mixtures. There is thus some evidence for an underlying similarity in mechanism.

TABLE II

ACTIVATION ENERGY

	$P^0_{NH_3}$ = 200 mm., $P^0_{O_2}$ = 100 mm.					
°C.	625	650	675	700	725	$E_{act.}$ kcal.
$[dP/dt]_0 \times 10^4$	52	69	109	213	361	42.2
t_{25}(sec.)	3850	1780	840	490	300	45.6
t_{50}(sec.)	11000	5860	2600	1500	800	46.9
	$P^0_{NH_3}$ = 100 mm., $P^0_{O_2}$ = 200 mm.					
°C	525	550	575	600	625	
$[dP/dt]_0 \times 10^4$	36	80	206	495	750	48.0
t_{25}	1650	730	340	160	90	42.7
t_{50}	4200	2100	910	380	190	44.2

Without attempting to trace what the detailed process may involve, one additional fact may be added. Current experiments in a KCl-coated reaction vessel indicate that with ammonia-rich mixtures the rates are the same as given above for the uncoated vessel, and conform to the second-order kinetics. On the lean side, the rate is relatively low in the early stages of reaction, and varies with the $P_{NH_3} \times P_{O_2}$ product. After a time, however, the rate begins to increase, and thereafter roughly duplicates data for uncoated vessels. The behavior is not unlike that associated with "cool-flame" phenomena in hydrocarbon combustion, except that there appear to be no real discontinuities. Possibly this is again a case of slow accumulation of an intermediate, such accumulation being facilitated in the uncoated vessel.

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The Mechanism of Decomposition of Borine Carbonyl

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The rates of decomposition of BH_3CO and BD_3CO, by a nearly homogeneous reaction of the type $2BH_3CO \rightleftarrows B_2H_6 + 2CO$, become intelligible on the assumption that the rate-determining step is $BH_3 + BH_3CO \rightarrow B_2H_6 + CO$, the BH_3 groups being furnished from the initial equilibrium $BH_3CO \rightleftarrows BH_3 + CO$. This mechanism implies a rate equation of the form $2kKt = \frac{x}{a-x} - \ln\frac{a}{a-x} = f(x)$, which is confirmed by linear graphs of f(x) *vs.* t for BH_3CO at 0–30° ($\log_{10} kK = 14.087 - 6000/T$) or for BD_3CO at 10–26° ($\log_{10} kK = 12.352 - 5370/T$). The corresponding ΔH values, 27.5 and 24.6 kcal., representing the sum of ΔH for the initial dissociation and ΔH for the activation of the rate-step, are rendered uncertain by a minor wall-reaction, small increases of kK with decreasing pressure, and the question of how well the first-step equilibrium is maintained. The equilibrium constants for the over-all decomposition are given by $\log_{10} K_{atm} = 7.104 - 1998/T$ ($\Delta F^\circ_T = 9142 - 32.5T$) for BH_3CO, and by $\log_{10} K_{atm} = 7.097 - 1850/T$ ($\Delta F^\circ_T = 8465 - 32.5T$) for BD_3CO, both in the range 25–80°. These imply that the decomposition-rate studies were not complicated by the reverse reactions, since the runs terminated at 8–25% decomposition.

The original description of borine carbonyl[1] included a preliminary study of the rate of the decomposition reaction $2BH_3CO \rightarrow B_2H_6 + 2CO$ (perfectly stoichiometric), with the suggestion that the first step might be the establishment of the equilibrium $BH_3CO \rightleftarrows BH_3 + CO$ as a very rapid process. The further suggestion that the rate-determining step might be $2BH_3 \rightarrow B_2H_6$ was not seriously inconsistent with the fairly rough original rate-data, but more recent studies have shown that a different theory of the rate-process is required.

The new data become orderly if it is assumed that the second step is $BH_3 + BH_3CO \rightarrow B_2H_6 + CO$, and that this step is so slow as not to have any serious effect upon the maintenance of equilibrium in the first step, $BH_3CO \rightleftarrows BH_3 + CO$. Thus if K is the equilibrium constant of the first step, and k the rate constant of the second, and it is noted that the total reaction yields two units of CO per unit of the rate-determining step, the rate equation is

$$\frac{dx}{dt} = 2kP_{BH_3CO}P_{BH_3} = \frac{2kK(P_{BH_3CO})^2}{P_{CO}} = \frac{2kK(a-x)^2}{x}$$

in which t is the time, a is the initial pressure, and x is the partial pressure of carbon monoxide (twice the observed increase of pressure, and equal to the loss of partial pressure of BH_3CO). Integrating between 0 and t, and 0 and x, gives the more usable form $2kKt = \frac{x}{a-x} - \log_e\frac{a}{a-x} = f(x)$.

It is recognized, of course, that this equation cannot describe the initial rate, because it implies that dx/dt is receding from infinity as the decomposition begins, and it is clear that the equilibrium $BH_3CO \rightleftarrows BH_3 + CO$ could not be maintained against a very rapid drain of BH_3 groups by the second step. Experimentally, it is very difficult to judge the nature of the early reaction, for the initial development of carbon monoxide is so fast even at 0° that the pressure a, corresponding to zero time, cannot be estimated directly. However, on termination of a run by freezing-out, the value of a may be determined from the measured volume of CO

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[1] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1937).