The Thermal Oxidation of Hydrazine Vapour.

By W. I. H. WINNING.

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The thermal gas-phase reaction between hydrazine and oxygen shows none of the chain characteristics of, *e.g.*, the hydrocarbon series. It is a predominantly surface reaction, the activation energy of which, below 100°, was found to be 6430 cal./mole.

On comparison with the absolute reaction-rate expression for a bimolecular surface reaction, unretarded by the products, and in which neither reactant is strongly adsorbed, very good agreement is obtained between the experimental and the theoretical rate value.

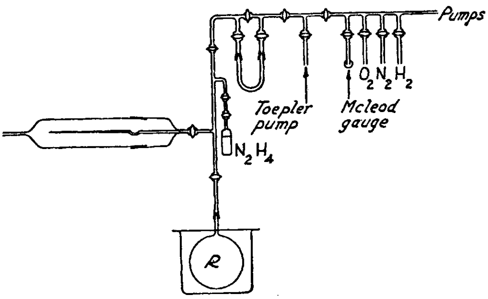
HYDRAZINE has recently received considerable prominence as a propellent, when combined with a suitable oxidiser (Audrieth and Ogg, " The Chemistry of Hydrazine," Wiley, New York, 1951). Surprisingly few data are available on its oxidation, and these are mainly concerned with the liquid-phase reaction. Two investigations have been made on the order of the vapour-phase reaction: in one, the rate was found to be of first order with respect to both hydrazine and oxygen, and proportional to the half-power of the water concentration (Nelson and Holcomb, U.S. Project Tech. Memo. No. PUR-7). In the other, Bowen and Birley (*Trans. Faraday Soc.*, 1951, **47**, 580) confirmed the initial first-order rate and suggested a mechanism for the reaction.

The present examination has been made primarily to measure the fundamental properties of the reaction, its velocity constants and activation energy, and to find whether it takes place in the gas phase or heterogeneously, and whether it possesses a chain mechanism or not. A value of the reaction order more in agreement with that of the second investigation has been assigned for the present conditions.

EXPERIMENTAL

A static system was set up, as shown diagrammatically in Fig. 1, in which the main reaction vessel, *R*, was a 2-l. quartz flask. To determine the effect of surface : volume ratio, two vessels were used, a similar one of Pyrex glass, and its ½-l. counterpart. These led directly to a manometer, with a glass-membrane gauge to prevent contamination of the reactants by mercury vapour. The hydrazine was stored nearby, after first being purified by distillation, and then transferred to a tube in the same manner. On the main gas line were attached a McLeod gauge and leads to the Toepler pump and gas-analysis section and to the gas storage bulbs.

FIG. 1.



Since hydrazine reacts slowly with oxygen even at room temperature, a sufficient variation in temperature was produced by an oil-bath, surrounding the reaction vessel and heated electrically.

In a typical run, the hydrazine was introduced from the side-tube, and its vapour pressure measured by the glass-membrane gauge. Oxygen was added immediately afterwards, at a pressure equal to, or in slight excess of, that required by the equation $N_2H_4 + O_2 = N_2 + 2H_2O$. In the experiments with water vapour, this was introduced immediately after the hydrazine. Nitrogen, when added as an inert gas, was the final substance to enter the vessel.

Reaction periods lay in the range from 3 to 300 min. The less volatile products were frozen out by a trap at −180°, situated between the reaction vessel and the Toepler pump. The nitrogen formed, which was the only product not to be removed in this way, could be collected and its volume measured, after combustion of the residual oxygen. The condensed products were dissolved in distilled water and titrated for total base and hydrazine itself with potassium iodate (Penneman and Audrieth, *Analyt. Chem.*, 1948, **20**, 1058). In this way, the presence of ammonia was unmistakably shown in the experiments conducted at the higher temperatures (Figs. 2 and 3).

Results.—(1) Early experiments with a small (100-ml.) vessel showed that adsorption effects were present, and that the surface played a considerable part in the reaction. In a 2-l. flask, results became more reproducible. Conditions eventually became steady, and it was in those circumstances that the data for determination of *k* and "*E* (apparent)" were obtained. The rates of disappearance of hydrazine were determined from the graphs, by tangents to the lines after various time intervals.

TABLE 1. *2-Litre vessel (quartz.)*

Temp.	Time * (min.)	$[N_2H_4]$ (unchanged) (10^4 mole/l.)	$-d[N_2H_4]/dt$ (10^4 mole $l.^{-1}$ $sec.^{-1}$)	k (l. $mole^{-1}$ $sec.^{-1}$)
185°	0	3·89	—	—
	5	2·57	—	—
	10	1·98	—	—
	10 (g)	1·87	2·17	6·21
	20	1·16	—	—
	20 (g)	1·13	0·78	6·11
	40	0·59	—	—
	40 (g)	0·57	0·20	6·15
185 (vessel KCl-coated)	0	4·37	—	—
	5	2·97	—	—
	12	2·10	—	—
	15	1·14	—	—
	25	0·65	—	—
115	0	4·80	—	—
	20	3·95	—	—
	25 (g)	3·55	0·83	0·659
	35	3·17	—	—
	50	3·20	—	—
	50 (g)	2·70	0·43	0·590
	100 (g)	1·80	0·20	0·616
	135	1·56	—	—
55	0	4·25	—	—
	40	3·22	—	—
	50 (g)	3·28	0·20	0·186
	90	3·03	—	—
	100 (g)	2·79	0·12	0·154
	150 (g)	2·50	0·083	0·133
	240	2·14	—	—
20	5	3·70	—	—
	5	3·39	—	—
	45	3·56	—	—
	80	3·12	—	—
	100 (g)	3·16	0·067	0·067
	120	3·20	—	—
	180	2·94	—	—
	250 (g)	2·65	0·057	0·069
	285	2·56	—	—

* (g) = Value from graph.

The extent of ammonia formation (expressed in the usual concentration units) at 115° and 185° is plotted in Figs. 2 and 3. That the effect was not due to decomposition of the hydrazine at the temperatures concerned was shown from the corresponding reaction in the absence of oxygen, and also with excess of nitrogen present, the hydrazine being quantitatively recovered.

When ln *k* was plotted against $1/T$ (Fig. 4), the apparent energy of activation of 8360 cal./mole was found for the temperature range 20—185°: between 20° and 115°, it is 6430 cal./mole.

(2) *Heterogeneity of the reaction.* Although certain previous results (Nelson and Holcomb, *loc. cit.*) were interpreted on the assumption of a homogeneous reaction, the effect of packing the vessel with glass-wool showed this not to be the case. It was found, however, that coating

FIG. 2.

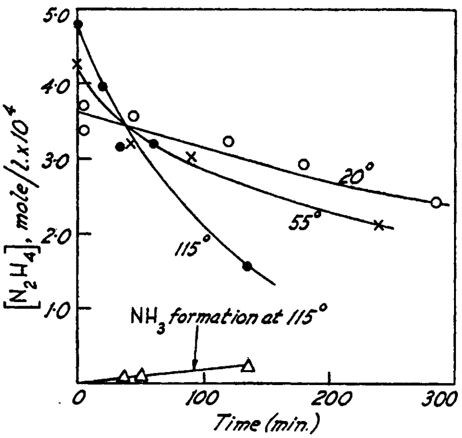
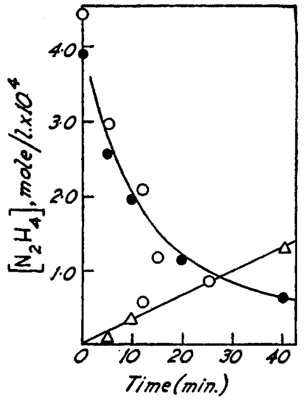


FIG. 3. *At* 185°.



● *Glass surface.*
○ KCl-*coated surface*
△ NH_3 *formation.*

FIG. 4.

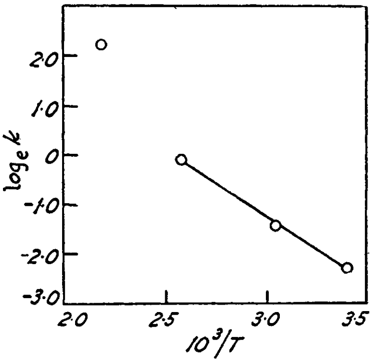
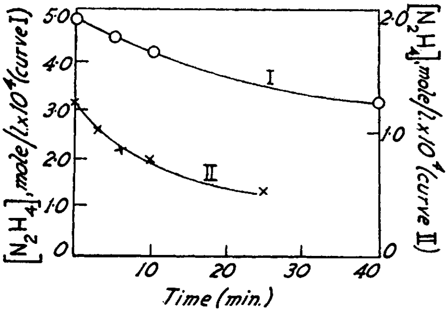


FIG. 5.



I, 2-*litre vessel.* II, ½-*litre vessel.*

FIG. 6.

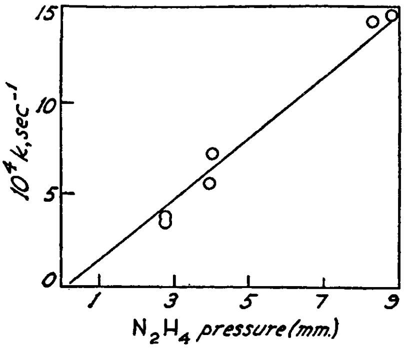
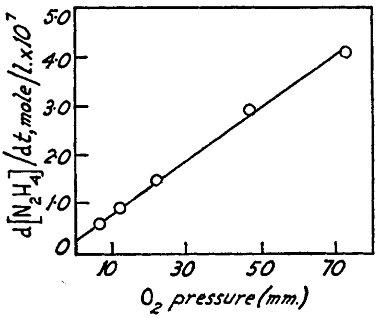


FIG. 7.



the surface with potassium chloride by the normal procedure, although exerting a strong retardation of the corresponding reaction with ammonia (Stephens and Pease, *J. Amer. Chem. Soc.*, 1950, **72**, 1188), left the rate unaffected in the present instance.

The effect of surface was investigated quantitatively by use of two Pyrex vessels, alike in all respects except volume. They were first carefully cleaned with concentrated nitric acid and distilled water, by an identical procedure. The rate agreed almost exactly with the theoretical value, direct proportionality to the surface area being assumed (Fig. 5 and Table 2). Hydrazine and oxygen pressures were again equated, within experimental limits.

TABLE 2. *Temperature* = 25°.

Time (min.)	$[N_2H_4]$ (unchanged) (10^4 mole/l.)	$-d[N_2H_4]/dt$ (10^7 mole l.$^{-1}$ sec.$^{-1}$)	k (l. mole^{-1} sec.$^{-1}$)	Time (min.)	$[N_2H_4]$ (unchanged) (10^4 mole/l.)	$-d[N_2H_4]/dt$ (10^7 mole l.$^{-1}$ sec.$^{-1}$)	k (l. mole^{-1} sec.$^{-1}$)
½-Litre vessel (Pyrex).				2-Litre vessel (Pyrex).			
0	1·26	—	—	0	4·90	—	—
3	1·03	—	—	5	4·53	—	—
5 (g)	0·93	0·71	0·770	10	4·15	—	—
6	0·89	—	—	10 (g)	4·16	0·86	0·474
10	0·80	—	—	20 (g)	3·69	0·65	0·477
10 (g)	0·75	0·42	0·740	30 (g)	3·34	0·50	0·448
15 (g)	0·63	0·29	0·731	40	3·13	—	—
25	0·54	—	—			Average value = 0·466	
		Average value = 0·747					

$$\frac{k\ (\tfrac{1}{2}\text{-l.})}{k\ (2\text{-l.})} = \frac{0{\cdot}747}{0{\cdot}466} = 1{\cdot}60. \qquad \frac{\text{Surface/volume}\ (\tfrac{1}{2}\text{-l.})}{\text{Surface/volume}\ (2\text{-l.})} = 1{\cdot}59.$$

(3) *Variation of hydrazine pressure.* With 2·7—8·8 mm. of hydrazine and excess (50 mm.) of oxygen, the times of half-conversion of the hydrazine were measured, and the first-order velocity constants derived. Direct proportionality between the rate and hydrazine concentration was found (Fig. 6 and Table 3).

TABLE 3. *Temperature* = 25°. 2-*Litre vessel* (*quartz*).

Initial oxygen concn. = $2{\cdot}94 \times 10^{-3}$ mole/l.

$[N_2H_4]$ (unchanged) (10^4 mole/l.)	Time (min.)	k (10^4 sec.$^{-1}$)	$[N_2H_4]$ (unchanged) (10^4 mole/l.)	Time (min.)	k (10^4 sec.$^{-1}$)
1·55	0	—	2·30	0	—
0·99	20	3·74	1·18	15	7·26
0·71	30	3·77			
			4·77	0	—
2·25	0	—	2·63	7	14·2
1·35	15	5·56			
			5·08	0	—
			2·13	10	14·5

(4) *Variation of oxygen pressure.* At a fixed hydrazine pressure (7·5 mm.), oxygen pressure was varied from 6·5 to 72·5 mm. The time of reaction was taken, so that the ΔN_2H_4 value lay consistently within a narrow range. The rate of reaction was in almost direct proportion to the oxygen concentration (Fig. 7 and Table 4).

TABLE 4. *Temperature* = 25°. 2-*Litre vessel* (*quartz*).

Initial hydrazine concn. = $4{\cdot}42 \times 10^{-4}$ mole/l.

$[O_2]$, mm.	Time (min.)	ΔN_2H_4 (10^4 mole/l.)	$-d[N_2H_4]/dt$ (10^7 mole l.$^{-1}$ sec.$^{-1}$)	$[O_2]$, mm.	Time (min.)	ΔN_2H_4 (10^4 mole/l.)	$-d[N_2H_4]/dt$ (10^7 mole l.$^{-1}$ sec.$^{-1}$)
6·5	70	2·60	(0·62)	47·5	15	2·59	2·88
12	50	2·79	0·93	72·5	10	2·46	4·10
22	30	2·64	1·47				

(5) *Effect of added nitrogen and water vapour.* No accelerating or retarding action was observed on the addition of excess of either substance (see Table 5).

TABLE 5. *Temperature* = 25°. 2-*Litre vessel* (*quartz*).

[Inert] gas], mm.	Time (min.)	ΔN_2H_4 (10^4 mole/l.)	$\dfrac{\Delta N_2H_4 \text{ (normal)}}{\Delta N_2H_4 \text{ (added gas)}}$	[Inert gas], mm.	Time (min.)	ΔN_2H_4 (10^4 mole/l.)	$\dfrac{\Delta N_2H_4 \text{ (normal)}}{\Delta N_2H_4 \text{ (added gas)}}$
Nitrogen.				Water vapour.			
Initial N_2H_4 concn. = $5{\cdot}77 \times 10^{-4}$ mole/l.				Initial N_2H_4 concn. = $2{\cdot}42 \times 10^{-4}$ mole/l.			
—	60	2·59	—	—	60	1·07	—
200	60	2·48	1·04	10	60	1·09	0·98
—	120	4·33	—	—	60	1·24	—
200	120	4·63	0·94	8	60	1·14	1·09

DISCUSSION

None of the criteria of a chain mechanism was observed at any stage in this investigation. Reaction appeared to commence immediately on mixing of the reactants, with no induction period. Addition of excess of the product gases did not affect the rate.

The rate increased linearly with the oxygen concentration, and this, taken in conjunction with other results, strongly suggests a non-chain bimolecular process.

When considered on this basis, in terms of the absolute reaction rate theory, the agreement between the theoretical and the experimental values was very good, particularly in comparison with other classical examples.

In confirmation of previous investigations (Bowen and Birley; Nelson and Holcomb; *locc. cit.*), the rate was shown to be of first order with respect to both oxygen and hydrazine, and independent of the nitrogen concentration. However, when an excess of water vapour was added, no increase in rate was observed, possibly owing to the very different experimental conditions.

That dimerisation of the hydrazine vapour might take place (Giguère and Rundle, *J. Amer. Chem. Soc.*, 1941, **63**, 1135) was considered, but the correspondence between the pressure of hydrazine as recorded on the manometer and the amount recovered by the method previously described excluded this at the temperatures and pressures concerned.

From the plot of ln k against $1/T$ (Fig. 4), a slightly greater activation energy is indicated at the higher temperature range (8·5 kcal./mole, to be compared with 6·5 below 100°). This can be accounted for if it is assumed that the gas-phase reaction is coming into effect: alternatively, it may be connected with the formation of small amounts of ammonia under these conditions. On the basis of a heat of activation of 38 kcal./mole, Bowen and Birley (*loc. cit.*) postulate the presence of short reaction chains as the operative mechanism.

The main results in the present work show a bimolecular surface reaction, unretarded by the products. They have been compared with the values obtained from the appropriate absolute reaction rate expression, in which the reactants are adsorbed to a comparable extent (Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw-Hill, New York, 1941), *viz.*,

$$v = \tfrac{1}{2} s C_{N_2H_4} C_{O_2} C_S \frac{\boldsymbol{k}T}{\boldsymbol{h}} \frac{f^*}{f_S} \frac{1}{F_{N_2H_4} F_{O_2}} e^{-\varepsilon_0/\boldsymbol{k}T}$$

When the terms for the partition functions of a non-linear polyatomic molecule and of oxygen are included, this becomes

$$v = \tfrac{1}{12} C_{N_2H_4} C_{O_2} C_S \frac{f_S}{f^*} \frac{\sigma_{N_2H_4}\sigma_{O_2}}{(\sigma^*)^2 (8\pi^2)^2} \frac{s^3 h^{10}}{(8\pi^3 ABC)^{\frac{1}{2}}\, I (2\pi m)^3\, (\boldsymbol{k}T)^{\frac{11}{2}}} e^{-\varepsilon_0/\boldsymbol{k}T}$$

the symbols possessing their usual significance (*op. cit.*).

With the generally accepted approximations in regard to the partition functions and symmetry numbers of the reactants and activated complex, and substitution of the values of the constants and other data, this becomes

$$v = \frac{2{\cdot}31 \times 10^{-3}}{T^{\frac{11}{2}}} [N_2H_4][O_2] e^{-E_0/\boldsymbol{R}T} \text{ mole cm.}^{-2} \text{ sec.}^{-1}$$

The corresponding rates from Table 1 are tabulated in Table 6 for the temperature 55°, under the heading $v_{\text{theor.}}$, along with the experimental rates, expressed in the same units for a reaction vessel of 2-l. capacity and 768 sq. cm. surface area. The value for the energy of activation (6430 cal./mole) from the results at the lower temperature range was preferred to the overall figure, for the reason previously adduced. No further modification was made for temperature.

TABLE 6. *Temperature* = 55°. 2-*Litre vessel* (*quartz*).

Initial N_2H_4 concn. = $5{\cdot}02 \times 10^{-4}$ mole/l.

Time, min.	50	100	150
$10^{13}v_{\text{expt.}}$, molecules cm.$^{-2}$ sec.$^{-1}$	5·2	3·1	2·2
$10^{13}v_{\text{theor.}}$, ,,	4·5	3·3	2·6

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FRICK CHEMICAL LABORATORY, PRINCETON, NEW JERSEY.
[Present address: MACLEANS LTD., BRENTFORD, MIDDLESEX.

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