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Oxidation Kinetics of Methylhydrazine in a Strictly Single-Phase Medium Studied in Reconstituted Air[1]

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Abstract—The oxidation of methylhydrazine (monomethylhydrazine MMH) is studied in a strictly single-phase gaseous medium, in a reconstituted surrounding atmosphere. In order to work under such conditions, a specific apparatus was assembled to monitor the evolution of the reactants through time. The reaction kinetics was studied at 50°C to avoid condensation of the water formed and for O_2/MMH mole ratios between 1 and 4. Under these conditions, the partial pressures of O_2 were between 0.05 and 0.18 bar (4% MMH per volume). The main reaction products were monitored through time and identified by gas chromatography coupled with mass spectrometry (GC/MS). The products were: N_2, CH_4, $CH_3{-}NH{-}N{=}CH_2$ (formaldehyde monomethylhydrazone), NH_3, H_2O, CH_3OH, and $CH_2{=}N{-}N{=}N{-}CH_3$ (2,3,4-triazapenta-1,3-diene). The formation of nitrosamines was not observed under these experimental conditions. The rate laws related to the disappearance of the reagents were clearly established and can be described by 2 consecutive parallel reactions of order 2 whose rate constants are: $k_1 = 7.57 \times 10^{-2}$ bar^{-1} min^{-1} and $k_2 = 0.5$ bar^{-1} min^{-1}. Analysis of the products permitted establishing an approximated balance of the global reaction.

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INTRODUCTION

Methylhydrazine (monomethylhydrazine MMH) is mainly used in the aerospace industry because of its hypergolic properties [1]. However, its oxidizability involves safety and quality control problems during transfer and storage. The objective of this work is to study the oxidation rate laws of MMH relating to atmospheric oxygen so as to simulate a possible leak of MMH in confined spaces such as closed systems (used in aircraft cockpits, submarines, etc.) by modelling MMH in a reconstituted atmosphere and to assert the absence of nitrosamines as they are highly toxic to humans.

The action of oxygen on MMH has been given much study, but analysis of the literature underlines the empirical nature of these studies. In particular, the use of measurements carried out in a two-phase medium (liquid-vapour) is difficult because of the superposition of the specific reaction mechanisms of each phase.

To obtain significant data, it is necessary to comply with precise experimental conditions and a rigorous operational protocol. Thus the study of the oxidation of MMH by oxygen was carried out in a strictly single-phase gaseous medium.

In a previous paper [2], a study carried out in a liquid single-phase medium led us to propose the following reaction scheme:

$$CH_3NHNH_2 + 2O_2 \longrightarrow 2NO + CH_3OH + H_2O.$$

In this paper, the oxidation of MMH is studied in a strictly gaseous single-phase medium. The different studies reported in the literature [3–7] indicate that reaction rates and the nature of the products seem to be closely related to experimental conditions (material of the reactor, surface activity, surface/volume ratio). The results are not readily usable because in most cases they were not quantified by equations or by clearly definite rate laws.

As the phenomena are complex, it is first necessary to design an experimental device to monitor the reaction in a strictly gaseous single-phase medium.

EXPERIMENTAL

Products and Analysis

Helium, oxygen, nitrogen and reconstituted air were provided by Air Liquide. Their purity was up to 99.995%. MMH of purity up to 98% was provided by Aldrich.

The analysis of the reagents and products was carried out by gas chromatography. The apparatus used was a Hewlett Packard 6890A chromatograph equipped with EPC (Electronic Pneumatic Control) modules to allow piloting and measuring gas flow rates and pressures. The data acquisition system was man-

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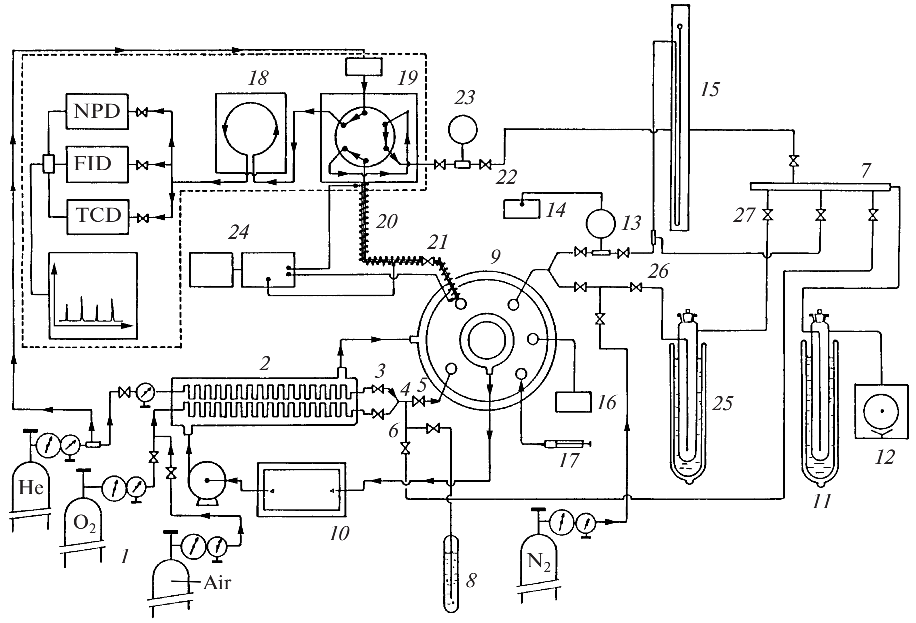


Fig. 1. Experimental set-up. *1*—compressed gas station, *2*—heat exchanger, *3*—two metallic valves, *4*—pipe common to the two valves, *5*—rotaflo valves in teflon, *6*—lateral tubulure, *7*—distribution ramp, *8*—wash-bottle, *9*—reactor, *10*—thermostatic fluid, *11*—trap with liquid air, *12*—vane pump, *13*—pressure sensor, *14*—numeric indicator associated to the pressure gauge, *15*—pressure sensor with mercury, *16*—chromel-alumel k thermocouple, *17*—hamilton gas syringe, *18*—capillary column of the chromatograph, *19*—programmable electro-pneumatic rotative six-way gas sampling valve, *20*—stainless steel pipe for gaseous samples before injection, *21* and *22* valves which allow isolating the pipe *20*, *23*—pressure gauge, *24*—temperature controller, *25*—traps assembled in series, *26* and *27* valves connecting the traps respectively to the reactor and to the distribution ramp *7*.

aged by Chemstation HP 3365 software. The injection system was of the Split/splitless type, allowing total or partial injection according to the concentration of the sample to be analyzed. The detection system was composed of 3 detectors: FID (flame ionization), NPD (nitrogen/phosphorus thermionic detector), TCD (thermal conductivity). The NPD detector was used together with the FID detector or the TCD detector to improve discrimination between the molecules that did and did not contain nitrogen atoms. Two different columns were used: HP5 trace (L: 30 m, internal diameter: 250 μm, film thickness: 0.25 μm) for trace analysis and HP-PLOT Molsieves 5A (L: 30 m, internal diameter: 320 μm, film thickness: 12 μm) to separate oxygen and nitrogen. The experimental conditions were as follows: injector at 250°C, detector at 250°C, carrier gas: He. For each column, the temperature sequence of the oven was programmed to obtain the best peak resolution:

HP5 trace: oven at 40°C—5°C/min—60°C—10°C/min—200°C (2 min);

MolSieves 5A: oven at 40°C (4 min)—15°C/min—200°C (2 min).

The flow rates of the carrier gas were respectively 7 and 3 ml/min.

The intermediate compounds were identified by gas chromatography coupled with mass spectrometry (GC/MS). The analyses were carried out with an HP 5890 series II/MSD 5970 apparatus. The column had the following characteristics: L: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm. Temperature: 30–200°C at 5°C/min.

Installation

The installation, which was designed and built at the laboratory, was composed of the following elements (Fig. 1).

—A compressed gas station (*1*) with helium, oxygen, reconstituted air and nitrogen was used to supply the reactor under a maximum pressure of 8 bar. The helium had a double function: it permitted supplying the chromatography and it avoided masking the nitrogen which can be generated by the oxidation of MMH.

—A heat exchanger (*2*) composed of 2 helicoidal serpentines enclosed in a thermostated jacket was used to distribute the gas (helium, oxygen, air or nitrogen) at the temperature of the reactor.

—A spherical borosilicate glass reactor (*9*) with double wall of a capacity of 4 l. The geometry was chosen to minimize the activity of the walls (surface/volume ratio). This reactor has *7* ports including: an MMH admission device, an opening for introducing a glass tube containing a halogen lamp to facilitate desorbing the walls, a pressure pick-up, a Chromel-Alumel thermocouple, a septum to extract or inject a vapour phase, an opening connecting to the chromatography via a pneumatic valve.

Table 1. Composition of the gaseous mixture according to the mass of monomethylhydrazine introduced into the reactor at $T = 25°C$

m_{MMH}, g	$P_{MMH} \times 10^2$, bar	$P_{O_2} \times 10^2$, bar	P_{He} (or P_{N_2}) $\times 10^2$, bar	Molar or volumetric composition			r
				MMH	O_2	He	
0.446	5.9	18.9	75.2	5.9	18.8	75.3	3.18
0.396	5.3	19.0	75.7	5.3	18.9	75.8	3.60
0.347	4.6	19.1	76.3	4.6	19.1	76.3	4.16
0.297	3.9	19.2	76.9	4.0	19.2	76.8	4.83
0.248	3.3	19.3	77.4	3.3	19.4	77.3	5.87
0.198	2.6	19.5	77.9	2.6	19.5	77.9	7.42
0.149	2.0	19.6	78.4	2.0	19.6	78.4	10.03
0.099	1.3	19.7	79.0	1.3	19.7	79.0	14.68
0.050	0.7	19.9	79.4	0.7	19.9	79.4	29.55
0.030	0.4	19.9	79.7	0.4	19.9	79.7	46.57

—A pumping station comprising a manifold (*7*), a trap with liquid air (*11*) and a vane pump (*12*), was used to apply a primary vacuum (10^{-3} Torr) throughout the installation.

—The absolute pressure in the reactor was measured by a thin layer high pressure sensor/AOIP (*13*) linked to a digital indicator ITI (*14*). The precision was 0.25% on the scale of the measurements (0–16 bar). The pressure could also be measured by a mercury manometer (*15*).

—A Chromel-Alumel K thermocouple linked to a digital temperature indicator AOIP/TNE (*16*) measured the temperature in the reactor to within 0.1°C.

—A vapour phase sampling and injection device. Two processes were used: a manual process using a Hamilton gas syringe (0–5 ml) via a septum (*17*), an automatic process, injecting the gaseous sample directly into the capillary column (*18*) through a programmable electro-pneumatic rotary six-way gas sampling valve (*19*). The gaseous sample was transferred toward the injection loop by expansion into a circuit under vacuum. This conduit was isolated from the reactor and the pumping station by valves (*21*) and (*22*). A Tacussel temperature regulator (*24*) linked to a differential thermocouple maintained the sampling system at a temperature equal or higher than those in reactor. This was necessary to avoid any condensation of the vapour phase during the sampling.

—A device for analysing the mixture by cryogenic transport: it was composed of 2 traps assembled in series (*25*), cooled by liquid nitrogen. The objective was to trap all the condensable products so as to increase the sensitivity of the chromatographic analyses.

More details are given in the caption of Fig. 1.

Operational Protocol

A specific operational protocol was established to ensure good reproducibility: the reactor was desorbed at 150°C for 3 h under vacuum, then nitrogen was introduced to eliminate humidity. A predetermined quantity of liquid MMH was introduced under an inert atmosphere in the tank designed for this purpose. The weight of MMH was calculated to give a partial pressure lower than its saturated vapour tension. The reagent was cooled with liquid air then the vacuum was applied. After withdrawal of the liquid air, MMH vaporized completely in the reactor, then helium was introduced. After flushing the system, oxygen was introduced to reach a pressure equal to atmospheric pressure. The evolution of the reaction mixture was monitored by reading the pressure and by gas chromatography.

To formulate the mixtures, it was necessary to know the density of MMH (d_{MMH}) and the saturated vapour tension of MMH (P_{MMH}):

$$d_{MMH} = 115034 - 9949 \times 10^{-4} T \, [8].$$

With T expressed in K.

Aston et al. [9] established the following relation:

$$\log P_{MMH} = 7.11158 - 1104.5711 \frac{1}{T} - \frac{152227.7}{T^2}.$$

T is expressed in K.

The two following tables (Tables 1 and 2) present the experimental conditions calculated to obtain a single-phase mixture saturated with MMH in a 4 l reactor at temperatures of 25 and 50°C, with a variable ratio $r = [O_2]/[MMH]$.

As oxygen is a much denser gas than helium, several experiments were carried out to determine the time needed to obtain a homogeneous mixture. Indeed, the mixture was homogeneous 3 min after the introduction of oxygen. To avoid this problem, a glass agitator driven by a magnetic drive was installed.

The calibration curves of oxygen, nitrogen, methane and methylhydrazine were carried out to quantitatively monitor the evolution of these 4 compounds according to time.

Table 2. Composition of the gaseous mixture according to the mass of monomethylhydrazine introduced into the reactor at $T = 50°C$

m_{MMH}, g	$P_{MMH} \times 10^2$, bar	$P_{O_2} \times 10^2$, bar	P_{He} (or P_{N_2}) $\times 10^2$, bar	Molar or volumetric composition			r
				MMH	O_2	He	
1.564	22.4	15.5	62.1	22.5	15.2	62.3	0.68
1.380	19.7	16.1	64.2	19.9	15.9	64.2	0.80
1.196	17.1	16.6	66.3	17.2	16.6	66.2	0.96
0.920	13.2	17.4	69.4	13.2	17.2	69.6	1.30
0.736	10.5	17.9	71.6	10.6	17.8	71.6	1.69
0.552	7.9	18.4	73.7	7.9	18.5	73.5	2.33
0.455	6.6	18.7	74.7	6.6	18.5	74.9	2.83
0.363	5.3	18.9	75.8	5.2	18.9	75.9	3.61
0.271	3.9	19.2	76.9	3.9	19.2	76.9	4.92
0.230	3.3	19.3	77.4	3.3	19.3	77.4	5.84
0.184	2.6	19.5	77.9	2.6	19.5	77.9	7.35
0.138	2.0	19.6	78.4	2.0	19.6	78.4	9.87
0.092	1.3	19.7	79.0	1.3	19.7	79.0	14.90
0.046	0.7	19.9	79.4	0.7	19.9	79.4	30.00
0.028	0.4	19.9	79.7	0.4	19.9	79.7	50.00

RESULTS AND DISCUSSION

Preliminary Study: Condensation Phenomena

The first experiments were carried out with excess oxygen ($r = [O_2]/[MMH] = 4$) at 25°C. The mass of monomethylhydrazine to be injected and the initial partial pressures of the reagents can be deduced by referring to Tables 1, 2. The experimental composition obtained was as follows: $P_{MMH} = 0.041$ bar ($m_{MMH} = 0.3085$ g), $P_{He} = 0.759$ bar, $P_{O_2} = 0.192$ bar. Indeed, $P_T = 0.995$ bar.

Under these conditions, a dense mist appeared, corresponding to the formation of formaldehyde monomethylhydrazone and water. The most probable reaction scheme is as follows:

$$8CH_3NHNH_2 + 6O_2 \longrightarrow CH_3NHN$$
$$= CH_2 + CH_4 + CH_3OH + 5N_2 + 11H_2O.$$

Table 3. Mass of MMH to be introduced to avoid water condensing at a given temperature

T, °C	$P^{water}_{s(T)}$, Torr	$P^{MMH}_{s(T)}$, Torr	m_{MMH}, g	m_{MMH} without regard for ν, g
25	23.8	46.1	0.17	0.49
30	31.8	64.3	0.22	0.63
35	41.2	83.3	0.29	0.80
40	55.3	106.9	0.38	1.01
45	71.9	135.7	0.48	1.26
50	92.5	170.9	0.61	1.56
55	118.0	213.3	0.77	1.92
60	149.4	264.1	0.96	2.34

In this case, the oxidation of MMH was not carried out in a strictly gaseous single-phase medium.

To avoid water condensation, it was necessary to introduce a mass of MMH corresponding to a partial pressure of the water formed during the reaction, lower than its saturated vapour pressure. By indicating the vapour pressure of the water at temperature T by $P^{H_2O}_{s(T)}$, we obtained the acceptable maximum quantity of water in the reactor of volume V_r:

$$m_{water} \le \frac{P^{water}_{s(T)} V_r}{RT} M_{water}.$$

By taking into account the stoichiometric coefficients (ν) relating to the reagents, the new mass of monomethylhydrazine to be injected becomes:

$$m_{MMH} \le \frac{\nu_{MMH}}{\nu_{water}} \frac{P^{water}_{s(T)} V_r}{RT} M_{water}.$$

The vapour pressures of water and MMH, between 25 and 60°C and the corresponding mass of MMH are indicated in Table 3. The values were calculated from these equations ($\nu_{MMH} = 8$; $\nu_{water} = 11$). The last column indicates the saturated mass of MMH taking into account the saturated vapour pressure of the reagents only.

In all cases, the following equation can be written:

$$\frac{\nu_{MMH}}{\nu_{water}} P^{water}_{s(T)} \le P^{MMH}_{s(T)}.$$

Oxidation of MMH in a Strictly Gaseous Medium ($T = 50°C$)

To remain below the water condensation limit, the oxidation of MMH was studied at 50°C for O_2/MMH ratios between 0.5 and 4. Under these conditions a weighed mass of MMH equal to 0.35 g was introduced in the reactor. The partial pressures of oxygen and helium were adjusted to obtain $P_T = 1$ bar. Gas chromatography (**GC**) permitted monitoring oxidation via a solenoid valve. All the condensable products were trapped and analyzed by GC at the end of the reaction.

Kinetic Modelling of Reagents

The variations through time of the partial pressure of the reagents (oxygen and MMH) and of the gaseous products (nitrogen and methane) were monitored by GC. It was necessary to carry out the reaction twice as not all the reagents could be analysed using the same column: MMH was analysed with the HP trace column, while the gases were analysed with the Molsieves 5A column.

Equimolar Oxidation Reaction of MMH

Tables 4a and 4b and Fig. 2 present the evolution through time of the partial pressures of O_2, N_2, CH_4, and MMH with the following initial conditions: $P_{MMH} = 0.052$ bar, $P_{O_2} = 0.063$ bar, $P_T = 1$ bar (0.0885 bar Helium) which corresponds to a ratio $r = P^0_{O_2}/P^0_{MMH} = 1.21$. The oxygen peak decreases, while nitrogen and methane appear.

The oxidation of MMH is a slow reaction. For the example presented in Fig. 2, the partial pressure of MMH was close to 0 bar only after 500 min. reaction time at which point the partial pressures of oxygen and nitrogen were respectively 0.028 and 0.034 bar. Complementary tests carried out for $1 < r < 4$ give similar results, i.e.:

$$\int_{0}^{P^{\infty}_{N_2}} dP_{N_2} = -\int_{P^{0}_{O_2}}^{P^{\infty}_{O_2}} dP_{O_2}$$

and

$$\int_{P^{0}_{MMH}}^{P^{\infty}_{MMH}} dP_{MMH} \approx \frac{2}{3}\int_{P^{0}_{O_2}}^{P^{\infty}_{O_2}} dP_{O_2}.$$

These stoichiometric relationships were verified only at the end of the reaction. Indeed, the instantaneous reactional balances defined by the Eqs. (1) and (2) varied from 3 to 1.5 for Eq. (1) and from 2 to 1 for Eq. (2) (Tables 5 and 6). The values 3 for Φ_1 and 2 for Φ_2 were obtained by extrapolation at $t = 0$.

$$\Phi^t_1 = \frac{P^0_{MMH} - P^t_{MMH}}{P^0_{O_2} - P^t_{O_2}} = \frac{\delta P^t_{MMH}}{\delta P^t_{O_2}} \qquad (1)$$

Table 4a. Oxidation kinetics of MMH. Evolution with the time of the partial pressures of O_2, N_2, and CH_4. Initial conditions: $P_{MMH} = 0.052$ bar, $P_{O_2} = 0.063$ bar, $P_T = 1$ bar, $T = 50°C$. Column Molsieves 5A

Time, min	$P_{O_2} \times 10^2$, bar	$P_{N_2} \times 10^2$, bar	$P_{CH_4} \times 10^2$, bar
5	6.10	0.25	0.20
26	5.70	1.30	0.25
47	5.20	1.68	0.28
76	4.75	2.05	0.28
100	4.35	2.37	0.27
201	3.47	3.07	0.29
229	3.30	3.13	0.30
270	3.25	3.17	0.30
293	3.17	3.20	0.30
343	3.10	3.25	0.30
386	3.07	3.28	0.35
548	2.95	3.36	0.35
710	2.88	3.41	0.35
887	2.84	3.41	0.35
1380	2.80	3.45	0.35

Table 4b. Oxidation Kinetics of MMH. Evolution through time of the partial pressure of MMH. Initial conditions: $P_{MMH} = 0.052$ bar, $P_{O_2} = 0.063$ bar, $P_T = 1$ bar, $T = 50°C$. Column HP5 Trace

Time, min	$P_{MMH} \times 10^2$, bar
2	4.36
24	3.90
49	2.95
78	2.10
200	0.70
272	0.44
310	0.32
500	0.00

Table 5. Oxidation kinetics of MMH. Evolution of the ratio of the quantities of MMH and oxygen consumed through time. Initial conditions: $P_{MMH} = 0.052$ bar, $P_{O_2} = 0.063$ bar, $P_T = 1$ bar, $T = 50°C$

Time, min	$P_{O_2} \times 10^2$, bar	$\delta P^t_{O_2} \times 10^2$, bar	$\delta P^t_{MMH} \times 10^2$, bar	Φ^t_1
0	6.30	0.00	0	
24	5.75	0.55	1.30	2.36
49	5.23	1.07	2.25	2.10
78	4.63	1.67	3.10	1.86
200	3.46	2.84	4.50	1.58
272	3.24	3.06	4.80	1.57
310	3.13	3.17	4.90	1.55

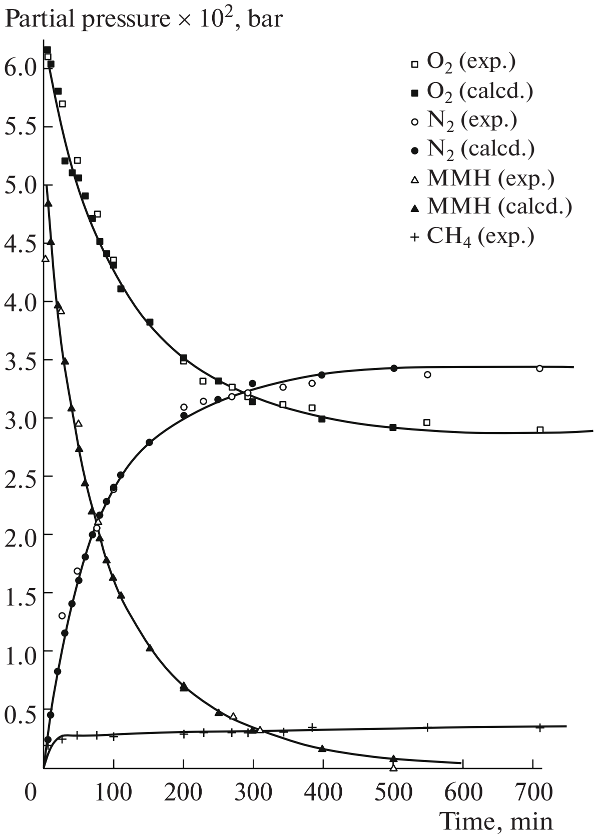


Fig. 2. Oxidation of MMH. Evolution of partial pressures of O_2, N_2, CH_4, MMH through time. Initial conditions: $P_{MMH} = 0.052$ bar, $P_{O_2} = 0.063$ bar, $P_T = 1$ bar, $T = 50°C$.

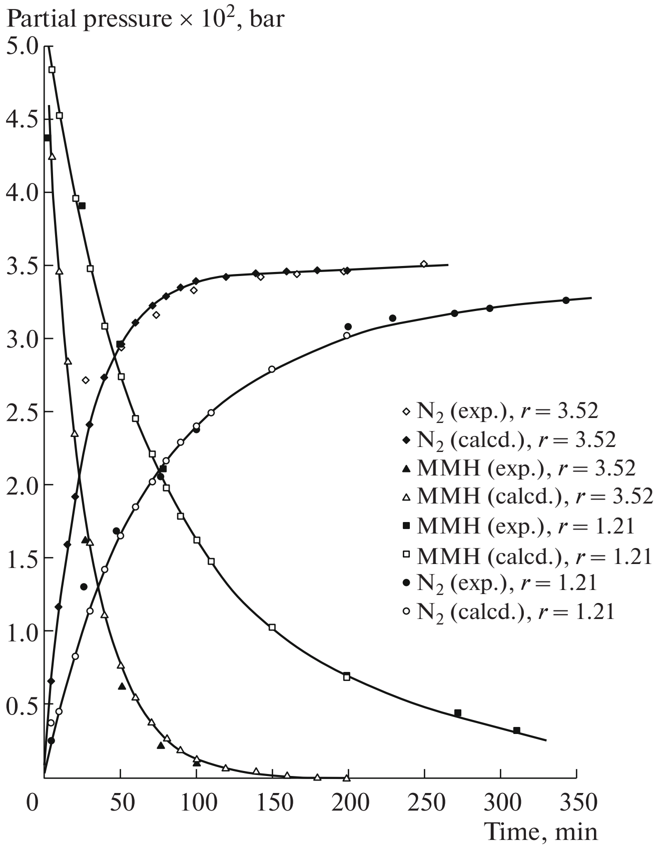


Fig. 3. Oxidation of MMH. Influence of the pressure of O_2 (r).

and

$$\Phi_2^t = \frac{P_{N_2}^t}{P_{O_2}^0 - P_{O_2}^t} = \frac{P_{N_2}^t}{\delta P_{O_2}^t}. \qquad (2)$$

The pressure of methane reached its maximal value at the beginning of the reaction and then remained constant.

These results can be explained by the existence of several elementary complex processes which can be described by the two following reactions:

$$3\mathrm{MMH} + O_2 \xrightarrow{k_1} Y + 2N_2 + \Sigma P_i, \qquad (I)$$

$$Y + O_2 \xrightarrow{k_2} \Sigma P_i, \qquad (II)$$

where k_1 and k_2 are the rate constants corresponding to the disappearance of O_2 and Y, which is an intermediate product. Its pressure P_Y corresponds to the following equation:

$$\frac{dP_Y}{dt} = k_1 P_{MMH}^{\alpha} P_{O_2}^{\beta} - k_2 P_Y^{\gamma} P_{O_2}^{\theta}.$$

A constant ratio between the consumed oxygen and the formed nitrogen was observed (cf. Φ_2). Under these conditions, three cases are possible:

(1) If $k_1 \gg k_2$, the reaction (II) is negligible and $\delta_{MMH}/\delta_{O_2} = 3$ whatever the level of progression of the reaction. This result does not correspond to the final stoichiometry observed.

(2) If $k_1 \ll k_2$, this implies a stoichiometry equal to 3/2 from the onset of the reaction. This result does not agree with the experimental values.

(3) Thus pressure P_Y is neither equal to 0, nor constant during the reaction. However, at $t = \infty$ Φ_1^{∞} and Φ_2^{∞} end respectively towards 3/2 and 1.

Solving the system implies knowing reaction orders α, β, γ, and θ, and by consequence, the initial partial pressures of the reagents.

Influence of Oxygen Pressure

For this study, the reaction was carried out under the same monomethylhydrazine temperature and pressure conditions ($P_{MMH}^0 = 0.052$ bar), but for a concentration of oxygen 3.5 times higher ($P_{O_2}^0$ = 0.184 bar). Figure 3 and Tables 7a and 7b present the evolution of partial pressures of MMH and nitrogen depending on time. Under these conditions, the rates of disappearance of MMH and formation of nitrogen are much faster. Contrary to the literature, the partial order referred to the oxygen was not equal to zero.

The order referred to β ($\alpha = 1$) was determined by measuring the slopes at the origin of the charts representing the partial pressures of MMH and N_2 according to time. When the reaction was carried out at the same initial pressure of MMH but for two values P^0_{a,O_2} and P^0_{b,O_2} corresponding to the oxygen pressure, the reaction rates at $t = 0$ were linked together by the following relations:

$$V^0_{a,N_2} = \left[\frac{dP_{N_2}}{dt}\right]_{a,t=0}$$

$$= -\frac{2}{3}\left[\frac{dP_{MMH}}{dt}\right]_{a,t=0} = 2k_1P^0_{MMH}\left[P^0_{a,O_2}\right]^{\beta},$$

$$V^0_{b,N_2} = \left[\frac{dP_{N_2}}{dt}\right]_{b,t=0}$$

$$= -\frac{2}{3}\left[\frac{dP_{MMH}}{dt}\right]_{b,t=0} = 2k_1P^0_{MMH}\left[P^0_{b,O_2}\right]^{\beta}.$$

From where β and k_1 were deduced:

$$\beta = \ln\frac{V^0_{a,N_2}}{V^0_{b,N_2}} \Big/ \ln\frac{P^0_{a,O_2}}{P^0_{b,O_2}}$$

and

$$k_1 = \frac{V^0_{a,N_2}}{2P^0_{MMH}[P^0_{a,O_2}]^{\beta}}.$$

When the reaction was carried out with equimolar reagents, the quantity of oxygen was too low to measure the initial rate with sufficient precision. Indeed, k_1 was determined by extrapolation of $P_{O_2} = f(t)$ at $t = 0$:

$$k_1 = \frac{-\left[\frac{dO_2}{dt}\right]_{t=0}}{P^0_{MMH}P^0_{O_2}}.$$

In the pressure range studied ($0.5 < r < 4$; $P^0_{MMH} = 0.052$ bar), β corresponded to a value between 0.90 and 1.20. The partial order carried over to β was considered as equal to 1 while k_1 was equal to 7.57×10^{-2} bar^{-1} min^{-1} at $T = 50°C$. As $R = 0.083$ l bar mol^{-1} K^{-1} (1 atm = 1.013 bar), k'_1 was expressed in l mol^{-1} min^{-1} by the relation:

$$k'_1 = k_1RT = 2.03 \text{ l mol}^{-1} \text{ min}^{-1} \text{ (at 50°C)}.$$

The kinetic parameters of the second step could be determined using a ratio r (great excess of MMH), leading to an initial step that was instantaneous compared to the second one. Under these conditions, the curve $P_{O_2} = f(t)$ only represented one interaction. However, to remain in an oxidant medium, we considered that the order in relation to Y and O_2 was equal to the unity. The validity of this hypothesis was demonstrated by an appropriate treatment.

Table 6. Oxidation kinetics of MMH. Evolution of the ratio of the quantities of formed nitrogen and consumed oxygen through time. Initial conditions: $P_{MMH} = 0.052$ bar, $P_{O_2} = 0.063$ bar, $P_T = 1$ bar, $T = 50°C$

Time, min	$\delta P^t_{N_2} \times 10^2$, bar	$\delta P^t_{O_2} \times 10^2$, bar	Φ^t_2
5	0.25	0.20	1.25
26	1.30	0.60	2.17
47	1.68	1.10	1.52
76	2.05	1.55	1.32
100	2.37	1.95	1.21
201	3.07	2.83	1.08
229	3.13	3.00	1.04
270	3.17	3.05	1.04
293	3.20	3.13	1.02
343	3.25	3.20	1.01
386	3.28	3.23	1.01
548	3.36	3.35	1.00

Determination of k_2

The partial instantaneous pressures of MMH, O_2, N_2, and Y are represented respectively by u, x, y_1, and y. Under these conditions at a given temperature, the oxidation of MMH in a gaseous medium is described by the following differential system:

$$\frac{dx}{dt} = k_1ux + k_2yx, \quad (3)$$

$$\frac{du}{dt} = 3k_1ux, \quad (4)$$

$$\frac{dy_1}{dt} = 2k_1ux, \quad (5)$$

$$\frac{dy}{dt} = k_1ux - k_2yx, \quad (6)$$

with the initial values $x = x_0$; $u = u_0$; and $y = y_0 = 0$.

t can be eliminated by Eqs. (3) and (4):

$$\frac{dx}{du} = \frac{1}{3}\left[1 + \frac{k_2}{k_1}\frac{y}{u}\right]. \quad (7)$$

Table 7a. Oxidation kinetics of MMH: Evolution of the pressure of nitrogen through time (initial conditions: $P_{\mathrm{MMH}} = 0.052$ bar, $P_{\mathrm{O}_2} = 0.063$ bar, $P_{\mathrm{T}} = 1$ bar, $T = 50°\mathrm{C}$

Time, min	5	27	50	73	98	120	143	167	198	250
$P_{\mathrm{N}_2} \times 10^2$, bar	0.65	2.70	2.93	3.15	3.32	3.41	3.42	3.43	3.45	3.50

Table 7b. Oxidation kinetics of MMH: Evolution of the pressure of MMH through time (initial conditions: $P_{\mathrm{MMH}} = 0.052$ bar, $P_{\mathrm{O}_2} = 0.063$ bar, $P_{\mathrm{T}} = 1$ bar, $T = 50°\mathrm{C}$

Time, min	5	27	51	76	100
$P_{\mathrm{MMH}} \times 10^2$, bar	4.23	1.62	0.62	0.22	<0.1

This equation can be integrated if $y = f(t)$ is expressed. It implies dividing Eq. (6) by Eq. (4) and writing $q = k_2/k_1$:

$$\frac{\mathrm{d}y}{\mathrm{d}u} = -\frac{1}{3} + \frac{q}{3}\frac{y}{u}.$$

By writing $y = \Phi(t)u$, a differential equation is obtained whose variables u and Φ can be separated:

$$\mathrm{d}(\ln u) = -\frac{\mathrm{d}\Phi}{1 - \Phi(q-3)}.$$

The following equation is obtained by integration ($t = 0$, $x = x_0$, and $u = u_0$):

$$\ln\frac{u}{u_0} = \frac{3}{q-3}\ln[1 - \Phi(q-3)].$$

Which, by using the initial variable, gives:

$$y = \frac{u}{q-3}\left[1 - \left(\frac{u}{u_0}\right)^{\frac{q-3}{3}}\right].$$

By substituting this expression in Eq. (7), a differential equation is obtained that depends only on variables x and u:

$$\frac{\mathrm{d}x}{\mathrm{d}u} = \frac{1}{3} + \frac{q}{3(q-3)}\left[1 - \left(\frac{u}{u_0}\right)^{\frac{q-3}{3}}\right].$$

Table 8. Oxidation kinetics of MMH: determination of the kinetic parameters of the second step of the reaction by solving Eq. (11)

Time, min	$P_{\mathrm{MMH}} \times 10^2$, bar	$P_{\mathrm{O}_2} \times 10^2$, bar	q	k_2, bar^{-1} min^{-1}
24	3.90	5.75	6.57	0.50
49	2.95	5.23	5.88	0.45
78	2.10	4.63	6.40	0.48
200	0.70	3.46	7.09	0.54
272	0.44	3.24	6.70	0.51
310	0.32	3.13	6.71	0.51

This equation permits obtaining the final expression which links the partial pressures of MMH and O_2 together:

$$x = x_0 - \frac{2q-3}{q-3}\left[\frac{u_0 - u}{3}\right] + \frac{u_0}{q-3}\left[1 - \left(\frac{u}{u_0}\right)^{\frac{q}{3}}\right]. \tag{8}$$

The second member of the Eq. (8) is denoted by $g(u_0, x_0, u, q)$. Points (x', u') are experimentally accessible depending on time for a fixed value of the initial pressures u_0 and x_0. If the preceding hypotheses are justified, for each moment t, a constant value q exists which is the solution of the following equation:

$$x' - g(u_0, x_0, u', x', q) = 0. \tag{9}$$

Table 8 gives the values q and k_2 for a reactional mixture whose initial pressures of O_2 and MMH are respectively 0.063 and 0.052 bar ($T = 50°\mathrm{C}$).

The variation of 16% between the extreme values is due to the experimental errors and to the fact that the pressures of MMH and O_2 were obtained by carrying out two different experiments. Indeed, k_2 was corrected by the following treatment:

Since u_0, x_0, and q are fixed for a given value of variable $u'(0 < u < u_0)$, the pressures of $\mathrm{O}_2(x)$, $\mathrm{N}_2(y_1)$ and the intermediary product $\mathrm{Y}(y)$ are deduced from the following relations:

$$x' = g(u_0, x_0, u', q),$$

$$y_1' = \frac{3}{2}(u_0 - u'),$$

$$y' = \frac{u'}{q-3}\left[1 - \left(\frac{u}{u_0}\right)^{\frac{q-3}{3}}\right].$$

Pressure u and consequently x, y_1, and y are linked to time by the following equation:

$$t = -\frac{1}{3k'}\int_{u_0}^{u'}\frac{\mathrm{d}u}{ug(u_0, x_0, q, u)}.$$

The results are presented in Fig. 3. There is good agreement between the experimental and calculated values ($T = 50°C$ and $q = 6.60$).

This permits obtaining:

$$k_2 = qk_1 = 0.50 \text{ bar}^{-1} \text{ min}^{-1},$$

$$k_2' = k_2RT = 13.4 \text{ l mol}^{-1} \text{ min}^{-1}.$$

Analysis of the Gaseous Medium

At the end of the reaction, after trapping the reactional medium, the samples were analysed by gas chromatography, permitting the identification of the major products. The discrimination between the molecules as a function of whether they contain nitrogen atoms or not is immediate, when comparing the "FID" and "NDP" analyses. To identify the different peaks, GC/MS analyses were carried out, highlighting a large number of peaks and indicating that the oxidation of MMH by oxygen is a complex reaction mechanism.

However, 4 major peaks were distinguished, corresponding to the following products:

0.67 min: CH_4, N_2, CH_3O, H_2O;

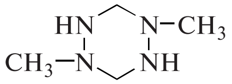
0.91 min: formaldehyde monomethylhydrazone (FMMH);

3.13 min: 2,3,4-triaza penta-1,3-diene ($CH_2{=}N{-}N{=}N{-}CH_3$);

4.90 min: 1,4-dimethyltetraza-1,2,4,5-cyclohexane.

This latter product ($\tau = 4.90$ min) can be formed by dimerization of FMMH:

$$2CH_3NHN{=}CH_2 \longrightarrow$$


,

$$M = 116 \text{ g mol}^{-1}.$$

This compound was not detected in situ during the reaction because of its very low saturation vapour pressure.

FMMH can be formed by dimerisation of 2 molecules of methyldiazene:

$$CH_3{-}N{=}NH + CH_3{-}N{=}NH$$
$$\longrightarrow CH_3 - NH{-}N{=}CH_2 + NH{=}NH,$$
$$M = 58 \text{ g mol}^{-1}.$$

Methyldiazene resulting from primary oxidation of MMH by oxygen:

$$2CH_3{-}NH{-}NH_2 + 1/2O_2$$
$$\longrightarrow 2CH_3{-}N{=}NH + 2H_2O,$$
$$M = 44 \text{ g mol}^{-1}.$$

Methyldiazene could be oxidized by O_2 to give methanol, methane and nitrogen:

$$2CH_3{-}N{=}NH \xrightarrow{1/2O_2} CH_3OH + CH_4 + 2N_2.$$

The analysis of the samples showed that no nitrosamines were formed during the oxidation of MMH under these experimental conditions.

The kinetic study and the identification of the products allowed us to propose the following reactional scheme in a reconstituted surrounding atmosphere:

$$9CH_3{-}NH{-}NH_2 + 6O_2 \longrightarrow 5N_2 + 2CH_4$$
$$+ \underset{\text{FMMH}}{2CH_3NH{-}N{=}CH_2} + NH_3 + 11H_2O$$
$$+ CH_3OH + CH_2{=}N{-}N{=}CH_3,$$
$$M = 71 \text{ g mol}^{-1}.$$

CONCLUSIONS

The oxidation of hydrazine and its two derivatives, unsymmetrical dimethyl hydrazine (UDMH) and MMH, was studied thoroughly in literature but the results are contradictory and show the complexity of the phenomena. To obtain reliable results it is necessary to define precise experimental conditions and rigorous operational protocols. Indeed, an experimental set-up was assembled to monitor the reaction in a strictly gaseous single-phase medium. It permitted monitoring the evolution of the reaction medium through time and detecting products formed even when they are only present in trace state. This set-up is original as the initial instant of the reaction is well defined: a known mass of MMH is vaporized under vacuum, then mixed with helium. Oxygen is injected under pressure. The homogeneity of the medium is obtained using a glass agitator rotated by a magnetic drive.

The kinetics of the reaction was studied at 50°C to prevent the water forming by condensation. The O_2/MMH ratios were between 1 and 4. Under these conditions, the partial pressures of O_2 were between 0.050 and 0.180 bar. The instantaneous reactional balances $\delta P^t_{\text{MMH}}/\delta P^t_{O_2}$ and $\delta P^t_{N_2}/\delta P^t_{O_2}$ were not constant through time and changed respectively from 3 to 1.5 and from 2 to 1.

The above results are explained by the occurrence of several inseparable complex processes, which can be viewed as the following two reactions:

$$3\text{MMH} + O_2 \xrightarrow{k_1} Y + 2N_2 + \Sigma P_i, \quad \text{(I)}$$

$$Y + O_2 \xrightarrow{k_2} \Sigma P_i, \quad \text{(II)}$$

where k_1 and k_2 are the rate constants, P_i designates the reaction products, and Y is the intermediate product. The partial pressure of the latter is given by the equation

$$\frac{dP_Y}{dt} = k_1 P^{\alpha}_{\text{MMH}} P^{\beta}_{O_2} - k_2 P^{\gamma}_{Y} P^{\theta}_{O_2}.$$

The reaction orders of the first step ($\alpha = \beta = 1$) were determined by the method of the initial rates, while those of the second step, by making hypotheses ($\gamma = \theta = 1$), were confirmed by an appropriate mathematical treatment. Indeed, contrary to the literature, no break in the kinetic curves or reactional orders varying through time were observed. In addition, the zero order referred to oxygen was not observed.

The rate constants have the following numerical values ($T = 50°C$):

$$k_1 = 7.57 \times 10^{-2}\ \text{bar}^{-1}\ \text{min}^{-1}$$

$$\text{or}\ \ k_1' = k_1RT = 2.03\ \text{l mol}^{-1}\ \text{min}^{-1},$$

$$k_2 = qk_1 = 0.50\ \text{bar}^{-1}\ \text{min}^{-1}$$

$$\text{or}\ \ k_2' = k_2RT = 13.4\ \text{l mol}^{-1}\ \text{min}^{-1}.$$

The GC/MS analyses permit asserting that no nitrosamines are formed during the oxidation of MMH and establishing the following reactional scheme:

$$9CH_3\text{–}NH\text{–}NH_2 + 6O_2 \longrightarrow 5N_2 + 2CH_4$$

$$+\ \underset{\text{FMMH}}{2CH_3NH\text{–}N{=}CH_2} + NH_3 + 11H_2O + CH_3OH$$

$$+\ CH_2{=}N\text{–}N{=}CH_3,$$

$$M = 71\ \text{g mol}^{-1}.$$

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