KINETICS OF THERMAL DECOMPOSITION OF HYDRAZINE AZIDE $N_2H_5N_3$

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We had shown previously [1-4] that the thermal decomposition of a number of hydrazine salts proceeds through equilibrium dissociation to hydrazine and the corresponding acid, and that the reaction rate is determined by the decomposition rate constant and equilibrium concentration of one of the dissociation products, specifically hydrazine in most of the compounds investigated. Sometimes the hydrazine interacts with the acid, reducing the hydrazine to ammonia. In the case of $N_2H_5N_3$ [1], the salt has a rather high volatility; the hydrazoic acid forming this salt is relatively weak, and the equilibrium is considerably shifted toward the original products. Moreover, HN_3 has good reducing properties. The kinetics and mechanism of the thermal decomposition of onium azides have been studied hardly at all; investigation of the decomposition of (I) is the starting point for such work.

EXPERIMENTAL

(I) was obtained by neutralizing an ether solution of HN_3 with an alcoholic solution of hydrazine, following procedures given in [5]. The resulting crystals were dried over P_2O_5. The content of N_2H_4 in the salt was determined by titration with iodine, following [6]; within the limits of error of the method (±0.2%), the N_2H_4 content matched the theoretical. The rate of thermal decomposition of (I) was investigated in a microcalorimeter [7] according to the rate of heat evolution in sealed glass ampuls, completely thermostated in the chamber of the calorimeter. With this experimental technique, all of the products that are formed remain in the ampul and are there distributed between the gas and liquid phases. The melting point of (I) is 75°C; the kinetics of the decomposition reaction were studied in the temperature interval 127.2-170°C, so that all experiments were performed in the liquid phase. The products, after the decomposition, were discharged for analysis into a gas cuvette, such that the final pressure of products in the cuvette was 0.02-0.04 bar (here, all of the reaction products passed into the gas phase), and the infrared spectrum was taken. Ammonia and hydrazine were found in the products, but no HN_3. The mass spectrum showed the presence of N_2 and the absence of H_2. Hydrazine was determined quantitatively by passing the gas through acidified water, followed by titration with iodine in accordance with [6].

DISCUSSION OF RESULTS

The reaction of thermal decomposition of (I) proceeds with a very slight autoacceleration, which is more appreciable at low temperatures. The initial reaction rate is considerably higher than in the case of N_2H_5Cl [3], but lower than the rate of decomposition of N_2H_5I [4]. The kinetic curves are described by a first-order autocatalytic equation

$$\frac{d\eta}{dt}=k_1(1-\eta)+k_2\eta(1-\eta)$$

where the values of k_1 and k_2 are on the same order of magnitude, and in some cases, $k_2 < k_1$.

In Table 1 we have listed the values of k_1 and k_2 for all of the temperatures investigated, and also the heats of reaction for thermal decomposition Q, obtained by numerical integration of the heat evolution rate curves. The mean value is $Q = 3.80 \pm 0.12$ kJ/g or 285 ± 8 kJ/mole.

The temperature dependences of the rate constants k_1 and k_2 are

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TABLE 1

T, °C	$m/v \cdot 10^3$, g/cm^3	$k_1 \cdot 10^4$, sec^{-1}	$k_2 \cdot 10^4$, sec^{-1}	Q, kJ/g
127,2	76	0,094	0,31	–
130,7	40,4	0,14	0,35	–
134,5	62	0,17	0,35	–
134,5	30,5	0,17	0,27	–
137,3	31	0,25	0,36	–
145,6	45	0,33	0,53	3,89
145,6	28	0,37	0,51	4,01
145,6	25	0,35		3,96
145,6	10	0,33		3,93
155,6	18	0,74	0,71	3,63
155,6	16	0,70	0,66	3,80
160,3	19	0,78	1,06	3,72
161,6	12	0,95	1,58	3,59
161,6	11	0,88	1,34	3,87
163,7	13	1,25	1,15	3,90
163,7	12	1,38	1,57	3,88
164,0	18	1,12	1,03	3,76
170,7	15	2,02		3,64

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*At temperatures below 145.6°C, the experiments were not brought to completion, and hence the heats of reaction were not measured.

$$k_1 = 10^{8,0} \exp\left(-\frac{100000}{RT}\right) \text{sec}^{-1}$$

$$k_2 = 10^{4,0} \exp\left(-\frac{67000}{RT}\right) \text{sec}^{-1}$$

The values of k_2 are less dependent on temperature than are the values of k_1; and with T > 170°C, the autocatalysis degenerates. A characteristic feature of the thermal decomposition of (I) in comparison with other hydrazine salts is the presence of the free N_2H_4 in the final products, in amounts of 0.22-0.27 mole per mole of (I); also, the products contain NH_3 and N_2; i.e., the decomposition proceeds mainly in accordance with the equation

$$N_2H_5N_3 = 0.25N_2H_4 + 1{,}33NH_3 + 1{,}58N_2$$

The calculated heat of this reaction is 288-297 kJ/mole at 25°C, which is very close to the values obtained experimentally at 145-170°C, thus confirming the correctness of selection of the equation for the decomposition reaction. Several experiments were performed on the thermal decomposition of hydrazine azide hydrazinate $N_2H_5N_3 \cdot N_2H_4$. The reaction rate was found to be considerably lower than for (I); at 157°C, the initial rate was $4.5 \cdot 10^{-6}$ sec^{-1}, and at 166°C, $13.7 \cdot 10^{-6}$ sec^{-1}. From a comparison with the data of Table 1, it can be seen that the initial rate dropped by a factor of 17-20; in the thermal decomposition of $N_2H_5NO_3$ and N_2H_5Cl, the rate increased when excess N_2H_4 was introduced [1-3]. The kinetic relationships observed in the thermal decomposition of (I) and the decrease in the rate when N_2H_4 was introduced indicate that the reaction, the same as for other hydrazine salts, proceeds through an equilibrium dissociation of the salt (I) in the liquid phase to form N_2H_4 and HN_3, and that the subsequent mechanism of decomposition is generally analogous to that of the decomposition of N_2H_5I [4]; the reaction rate is determined by the rate of interaction of the original salt with a molecule of HN_3 formed by dissociation

$$\begin{array}{ccccc} N_2H_5N_3{}^{l} & \rightleftarrows & N_2H_4{}^{l} & + & HN_3{}^{l} \\ & & \uparrow\downarrow & & \uparrow\downarrow \\ & & N_2H_4{}^{g} & & HN_3{}^{g} \end{array} \qquad (1)$$

$$N_2H_5N_3 + HN_3 \rightarrow 2NH_3 + 3N_2$$

$$-\frac{dc_{(I)}}{dt} = k_3 \cdot c_{(I)} \cdot c_{HN_3}; \; k_1 = k_3 \cdot c^0_{(I)} c^0_{HN_3} \qquad (2)$$

where $c^{0}_{(I)}$ and $c^{0}_{HN_3}$ are the initial concentrations of the salt and the acid in the melt of (I). The decomposition of HN_3 in such a system is very improbable, since this reaction proceeds in the gas phase at an appreciable rate only at temperatures of 260-280°C [8]. No data are available on the thermal stability of HN_3 in the liquid phase, but its decomposition should evidently lead to the appearance of H_2 in the reaction products, and we did not observe this.

The main difference between the decomposition of (I) and that of N_2H_5I is that the N_2 formed in reaction (2) is not capable of oxidizing hydrazine, as is the case for iodine in the decomposition of N_2H_5I [4]. Therefore, hydrazine accumulates in the system, and it is one of the final products of the reaction. The decomposition proceeds at higher temperatures than for the N_2H_5I; and, owing to the accumulation of hydrazine, the concentration of the complexes $N_2H_4 \cdot N_2H_5^+$ is much higher.

The thermal decomposition of these complexes, which is the limiting stage in the decomposition of $N_2H_5NO_3$ and N_2H_5Cl, becomes appreciable in the case of (I) as well, since the final content of hydrazine is only half of what it should be if the decomposition proceeded only in accordance with reactions (1) and (2), i.e., the thermal decomposition of the complexes ends when the $N_2H_5^+$ ions disappear in the system.

The second difference is that the vapor pressure over (I) is very high in comparison with that over other hydrazine salts; this is related to the relatively low acidity and high volatility of HN_3. The equilibrium vapor pressure of ($HN_3 + N_2H_4$) over (I) at 160°C is about 0.7 bar; in the case of $N_2H_5NO_3$ and N_2H_5Cl, the vapor pressure at 200°C is no more than 0.001 bar. Most of the NH_3 formed in reaction (1) exists in the gas phase; its concentration in the liquid phase is determined by the equilibrium pressure and solubility; the solubility drops off with increasing temperature. Thus, the rate constant k_1 includes the equilibrium concentration of HN_3 in the liquid phase; its activation energy is reduced by the heat of vaporization of HN_3 ($E = 100$ kJ/mole in comparison with 137 kJ/mole for N_2H_5I); and the preexponential factor is reduced by the corresponding change in entropy of vaporization. The change in enthalpy upon vaporization of pure HN_3 is 30 kJ/mole [9]. Of course, the kinetic parameters of the reactions of interaction of HN_3 and HI with the corresponding molecules must differ from each other, and there can be no complete agreement. During the course of the process, N_2H_4 and NH_3 accumulate, and the rate should drop off owing to the decrease in the equilibrium concentration of HN_3. The slight autocatalysis observed in the initial stages is probably related to catalysis of reaction (2) by some intermediate product, which we have not been successful in isolating. Another possible reason for the acceleration of the reaction is an increase in the dielectric constant of the medium during the course of the process, with a corresponding change in the equilibrium of dissociation.

The additional molecule of N_2H_4 in the solvate $N_2H_5N_3 \cdot N_2H_4$ reduces the equilibrium concentration of HN_3 very sharply and thereby suppresses reaction (2); the initial rate is determined almost entirely by the decomposition of the complexes $N_2H_4 \cdot N_2H_5^+$. For such a reaction,

$$-\frac{dc_{(I)}}{dt}=k_4\cdot c_{N_2H_5^+}\cdot c_{N_2H_4}$$

Assuming that in a melt of $N_2H_5N_3 \cdot N_2H_4$ $c_{N_2H_5^+} = c_{N_2H_4} \approx 12$ moles/liter, we have, at 157°C, $k_4 = 3.8 \cdot 10^{-7}$ liter · mole^{-1} · sec^{-1}, and for 166°C, $k_4 = 11.4 \cdot 10^{-7}$ liter · mole^{-1} · sec^{-1}, these values being very close to those obtained in [1] for the rate constant in the decomposition of the complex $N_2H_4 \cdot N_2H_5^+$. In the course of the reaction, the hydrazine concentration drops off, and reaction (2) becomes possible; however, along with this, the concentration of the NH_3 that is the final product increases, and hence c_{HN_3} remains low, and the decomposition rate also remains relatively low. Thus, the complexation of (I) with a molecule of N_2H_4 leads to a change in the mechanism of thermal decomposition and a substantial increase in its thermal stability.

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CONCLUSIONS

1. The kinetic parameters have been obtained for the reaction of thermal decomposition of $N_2H_5N_3$ in the liquid phase.

2. The thermal decomposition of $N_2H_5N_3$ proceeds through preliminary dissociation into N_2H_4 and HN_3; the reaction rate is determined by the rate of interaction of $N_2H_5N_3$ and HN_3.

3. The introduction of an N_2H_4 molecule into the $N_2H_5N_3$ leads to a change in the decomposition mechanism; the decomposition of complex ions $N_2H_4 \cdot N_2H_5^+$ becomes decisive.

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FORMATION OF FREE RADICALS IN REACTION OF CUMYL HYDROPEROXIDE WITH SULFUR-CONTAINING CHELATE OF COBALT

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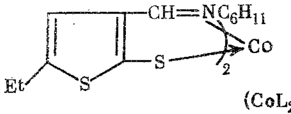
Sulfur-containing chelates of metals are used as inhibitors of hydrocarbon oxidation processes [1-3]. The antioxidant effect related to their participation in chain-breaking is often reduced as a result of the simultaneous occurrence of catalyzed decomposition of hydroperoxides into free radicals (this is the dual function of metal compounds) [4, 5].

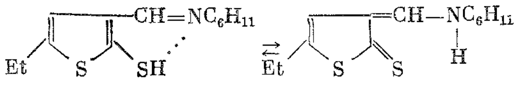
Here we are reporting on a study of the formation of free radicals by the interaction of a cobalt chelate having S and N atoms in the chelate unit, or the corresponding free ligand, with cumyl hydroperoxide (the undesirable direction for the inhibiting effect of the chelate).

EXPERIMENTAL

In this work we used cumyl hydroperoxide (CHP), a cobalt chelate (CoL_2), and the free ligand (LH):



(CoL₂)



(LH)

The reaction of CHP with CoL_2 or LH in chlorobenzene solution was carried out at 10-50°C in air. The CHP concentration was determined iodometrically. The free radical formation rate was determined by the use of a nontraditional acceptor — the polyene hydrocarbon β-carotene (a) and the nitroxyl radical 4-methyl-2-spirocyclohexyl-3,4,2',3'-tetrahydrofurano-1,2,3,4-tetrahydroquinolin-1-oxyl ($\geq NO^\cdot$). In the case of the nitroxyl, analyses were made to determine the accumulation of the quinone-nitrone (Q), which is formed by the interaction of ($>NO^\cdot$) with peroxy radicals [6].

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