Mechanism of thermal decomposition of diphenyldiazomethane in the presence of oxygen

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The kinetics, products, and mechanism of thermal decomposition of diphenyldiazomethane (RN_2, R = Ph_2C) in the presence of oxygen were studied. Thermolysis is accompanied by chemiluminescence. An emitter of chemiluminescence (^3RO) forms in the reaction of benzophenone *O*-oxide $RO\dot{O}$ with RN_2.

Key words: diazo compounds, carbonyl-oxides; chemiluminescence, thermal decomposition.

Thermal decomposition of diazo compounds in the presence of oxygen is a convenient procedure for the preparation and study of chemical conversions of carbonyl oxides, which are intermediates of ozonolysis of olefins.[1,2]

Previously,[3] using thermolysis of diphenyldiazomethane as an example, it has been demonstrated that this reaction is accompanied by chemiluminescence. The triplet excited benzophenone $^3R{=}O$ (R = Ph_2C) is the emitter of this reaction. In this work, we studied the kinetics and products of the decomposition of RN_2, determined the stage of chemiexcitation, and suggested a mechanism of the process.

Experimental

Acetonitrile and *o*-dichlorobenzene were purified according to standard procedures.[4] RN_2 was synthesized and purified according to the procedure reported previously.[5] Benzophenone azine (RN_2R) was prepared according to the known procedure.[6]

Concentrations of RN_2 and RN_2R were determined spectrophotometrically at λ_{max} = 525 nm (ε 130 L mol^{-1} cm^{-1}) and 484 nm (ε 600 L mol^{-1} cm^{-1}), respectively (for RN_2 at 484 nm and RN_2R at 525 nm, the extinction coefficients are 70 and 10 L mol^{-1} cm^{-1}, respectively). Benzophenone was determined by GLC (150—200 °C, 10% SE-30 on Chromaton N-AW).

After saturation of acetonitrile with air at 75 °C, the concentration of oxygen ($0.7 \cdot 10^{-3}$ mol L^{-1}) dissolved in acetonitrile was calculated according to the known procedure.[7]

The kinetics of consumption of RN_2 was studied with the use of a temperature-controlled glass cell placed into the cell chamber of a spectrophotometer. A temperature-controlled glass reactor equipped with a reflux condenser and a thermocouple was placed into a chemiluminescence device (a lightproof chamber). FEU-39 or FEU-148 were used as a detector of radiation.

All kinetic and chemiluminescence experiments were carried out at 75 °C in a MeCN solution with continuous supply of the reaction mixture with air or an O_2—Ar gas mixture.

Results and Discussion

Combustion products. The major products of the decomposition of RN_2 in the presence of O_2 are R=O and RN_2R (Table 1). Their yields depend little on the type of the process (photolysis or thermolysis), the solvent, and the temperature and substantially depend on the ratios of the initial concentrations ($[O_2]_0/[RN_2]_0$). The yield of R=O increases, the yield of RN_2R de-

Table 1. Dependences of the yields of R=O and RN_2R upon decomposition of RN_2 under an atmosphere of O_2 on the experimental conditions

Solvent	*T*/°C	$[RN_2]_0$ /mol L^{-1}	Yield (mol.%)		Reference
			R=O	RNN_2R	
		Photochemical decomposition			
C_6H_{12}	-20	0.125	56	10	8
C_6H_6	-20	0.125	68	11	8
C_6H_{12}—C_6D_{12}	26	$2.4 \cdot 10^{-2}$	82	Traces	9
$C_6H_5CH_3$—$C_6D_5CD_3$	26	$1.6 \cdot 10^{-2}$	83	Traces	10
CH_3CN	-20	$\sim 10^{-3}$	97	3	11
		Thermal decomposition			
C_6H_5Cl	80	0.05	70	30	12
o-$C_6H_4Cl_2$*	85	$1.2 \cdot 10^{-3}$	76	22	This work
o-$C_6H_4Cl_2$	85	$5.7 \cdot 10^{-3}$	84	9	The same
o-$C_6H_4Cl_2$	85	$2.3 \cdot 10^{-3}$	89	8	«
o-$C_6H_4Cl_2$	85	$1.2 \cdot 10^{-3}$	90	7	«

* In air.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 276—279, February, 1997.

1066-5285/97/4602-0261 $18.00 © 1997 Plenum Publishing Corporation

creases, and the total yield of the products becomes approximately quantitative as the $[O_2]_0/[RN_2]_0$ increases.

Kinetics of consumption of RN_2. Kinetic experiments were carried out at $[O_2]_0 = 0.7 \cdot 10^{-3}$ mol L^{-1} and rather low values of $[RN_2]_0$, *i.e.*, under conditions in which R=O is the major product of the reaction.

Kinetic curves of consumption of diazoalkane are readily linearized on the coordinates of the equation $\ln([RN_2]_0/[RN_2]) = k_{sp}t$ (the conversion was 70—80%); whence it follows that the kinetics of consumption of RN_2 obeys the first-order equation:

$$-d[RN_2]/dt = k_{sp}[RN_2]. \qquad (1)$$

The results of spectrophotometrical determination of the rate constant k_{sp} at various initial concentrations $[RN_2]_0$ are given below:

$[RN_2]_0 \cdot 10^3$/mol L^{-1}	0.8	2.0	7.4	15.0
$k_{sp} \cdot 10^4$/s^{-1}	2.6	2.7	2.8	2.7

Chemiluminescence upon thermal decomposition of RN_2. The relationship between initial intensities of chemiluminescence (I_0) and $[RN_2]_0$ was studied under an atmosphere of O_2—Ar (1 : 1). At rather low initial concentrations of the substrate, the value of I_0 increases as the concentration $[RN_2]_0$ increases:

$[RN_2]_0 \cdot 10^4$/mol L^{-1}	0.9	1.7	2.2	4.4	8.8	11.0
I_0/rel.unit	17	29	35	72	108	117

When $[O_2]_0/[RN_2]_0 \geq 1.9$, this dependence is linear (the correlation coefficient is 0.99). The concentration of O_2 in a solution was calculated on the assumption that its solubility obeys Henry's law.

The kinetics of chemiluminescence decay was studied in the region of the linear dependence of I_0 on $[RN_2]_0$. The process was characterized by the effective first-order rate constant k_{CL}, which was calculated from the initial regions of the kinetic curves of decay according to the following equation:

$$\ln(I_0/I) = k_{CL}t, \qquad (2)$$

where I is the current intensity of chemiluminescence.

It was established that at $[RN_2]_0 = 1.0 \cdot 10^{-4}$ and $4 \cdot 10^{-4}$ mol L^{-1}, k_{CL} are $2.6 \cdot 10^{-4}$ and $2.4 \cdot 10^{-4}$ s^{-1}, respectively.

Mechanism of the process. Based on the experimental results and the published data,[11,13–23] the following mechanism of the process at the initial stage (the first-order rate constants are given in s^{-1}, the second-order rate constants are given in L mol^{-1} s^{-1}) can be suggested.

Scheme 1

(0) $RN_2 \longrightarrow {}^1R + N_2$

(ST, TS) ${}^1R \rightleftharpoons {}^3R$ $\quad k_{ST} = 3.2 \cdot 10^9$ [15,16]; $k_{TS} = 6.3 \cdot 10^6$ [16]

(1) ${}^1R + RN_2 \longrightarrow R{=}N{-}N{=}R$ $\quad k_1 = 2.3 \cdot 10^{10}$ [17]

(2.1) ${}^3R + RN_2 \longrightarrow R{=}N{-}N{=}R$ $\quad k_{21} = 3.4 \cdot 10^7$ [17]

(2.2) ${}^3R + O_2 \longrightarrow \dot{R}O\dot{O}$ $\quad k_{22} = 5 \cdot 10^9$ [18,19]

(3.1) $\dot{R}O\dot{O} + RN_2 \longrightarrow R{=}O,\ {}^3R{=}O + N_2$ $\quad k_{31} = 4 \cdot 10^5$ [18]

(3.2) $\dot{R}O\dot{O} + \dot{R}O\dot{O} \longrightarrow 2\,R{=}O + O_2$ $\quad 2k_{32} \approx (3–9) \cdot 10^7$ [19,11]

(4.0) ${}^3R{=}O \longrightarrow R{=}O,\ h\nu$ $\quad k_{40} \sim 10^4–10^5$ [13,20]

(4.1) ${}^3R{=}O + RN_2 \longrightarrow R{=}O + RN_2$

 ${}^3R{=}O + RN_2 \longrightarrow {}^3R + R{=}O + N_2$

(4.2) ${}^3R{=}O + O_2 \longrightarrow R{=}O + O_2,\ {}^1O_2$ $\quad k_{42} = (2–3) \cdot 10^9$ [21,22]

(5.0) ${}^1O_2 \longrightarrow O_2$ $\quad k_{50} \approx 2 \cdot 10^4$ [23]

(5.1) ${}^1O_2 + RN_2 \longrightarrow \dot{R}O\dot{O} + N_2$ $\quad k_{51} = 1 \cdot 10^9$ [19]

Reactions (0)—(3.2) (without a channel of formation of ${}^3R{=}O$) were considered in the literature many times as elementary stages of the mechanism of photolysis and thermolysis of RN_2 in the presence of oxygen. Reactions (4.0)—(5.1) were included in the scheme of the process because chemiluminescence was observed upon decomposition of RN_2.

It is necessary to make some comments on Scheme 1.

1. Under our experimental conditions, reactions of ${}^1R$, ${}^3R$, and ${}^3R{=}O$ with MeCN are negligibly slow,[13,14] and, therefore, they are not included in the scheme of the process.

2. Because of very high rate constants k_{ST}, k_1, k_{22}, and k_{42}, the following competitive reactions may be ignored: ${}^1R \xrightarrow{O_2} {}^3R$, recombination of ${}^1R$ and ${}^3R$, and annihilation of ${}^3R{=}O$.[13,14]

3. The reaction ${}^1R + O_2 \longrightarrow \dot{R}O\dot{O}$ is spin forbidden. This reaction either does not actually occur[18] or is very slow.[1]

4. Isomerization of $\dot{R}O\dot{O}$ to the corresponding dioxirane requires a rather high activation energy (20—30 kcal mol^{-1}).[24] Under our experimental conditions, this reaction does not proceed to a large degree, which is also evidenced by the composition of the thermolysis products.

5. Apparently, ${}^3R$ forms by the reaction of ${}^3R{=}O$ with RN_2 through the stage of formation of the excited dissociation ${}^3RN_2$ intermediate.

Based on the rate constants given in Scheme 1, it can be demonstrated that in a steady-state mode under the conditions of our experiment ($[RN_2]_0 \sim 10^{-4}-10^{-2}$ and $[O_2]_0 \sim 10^{-3}$ mol L^{-1}), the following relationships are fulfilled:

$$k_{ST} \gg k_{11}[RN_2],\ k_{22}[O_2] \gg k_{21}[RN_2],$$
$$k_{31}[RN_2] \gg 2k_{32}[\dot{R}O\dot{O}];\ k_{31}[\dot{R}O\dot{O}] \gg k_1[{}^1R],$$
$$k_{31}[\dot{R}O\dot{O}\,] \gg k_{21}[{}^3R],\ k_{42}[O_2] \gg k_{40};\ k_{51}[RN_2] \gg k_{50}. \quad (3)$$

The conclusion that reaction (3.1) proceeds substantially faster than reactions (1) and (2.1) (see Scheme 1) is also confirmed by the composition of products of the thermolysis of RN_2 (the yield of ketone is substantially larger that the yield of azine).

Kinetics of consumption of RN_2. According to the mechanism suggested above,

$$-d[RN_2]/dt = k_{RN_2}[RN_2], \quad (4)$$

where $k_{RN_2} = k_0 + k_{11}[{}^1R] + k_{21}[{}^3R] + k_{31}[\dot{R}O\dot{O}] + \Phi_{41}k_{41}[{}^3R{=}O] + k_{51}[{}^1O_2]$
or, taking into account Eq. (3),

$$k_{RN_2} = k_0 + k_{31}[\dot{R}O\dot{O}] + \Phi_{41}k_{41}[{}^3R{=}O] + k_{51}[{}^1O_2].$$

By substituting steady concentrations $[\dot{R}O\dot{O}]$, $[{}^3R{=}O]$, and $[{}^1O_2]$, which were determined taking into account relationships (3), we obtain

$$k_{RN_2} = \frac{2k_0}{1-\Phi}.$$

Here

$$\Phi = \Phi_{31}\Phi_{41}\alpha_{41} + \Phi_{31}\Phi_{42}\alpha_{42},$$
$$\alpha_{41} = k_{41}[RN_2]/(k_{41}[RN_2] + k_{42}[O_2]),$$
$$\alpha_{42} = k_{42}[O_2]/(k_{41}[RN_2] + k_{42}[O_2]) = 1 - \alpha_{41}.$$

Φ_{31}, Φ_{41}, and $\Phi_{42} = 0.29$ [21] are the quantum yields of excitation of $^3R{=}O$ in (3.1) and formation of ^3R and $^1O_2$ in reactions (4.1) and (4.2), respectively.

When $[RN_2]_0/[O_2]_0$ changes by a factor of ~15, the experimental value of k_{RN_2} remains virtually unchanged. This suggests that $\Phi \ll 1$, and, therefore,

$$k_{RN_2} \approx 2k_0. \quad (5)$$

Stage of chemiexcitation and the kinetics of chemiluminescence decay. Triplet excited $^3R{=}O$ molecules can be generated in exothermic reactions (3.1) and (3.2). According to the procedure reported previously,[25] $\Delta H_{3.2} = -76$ kcal mol^{-1}. The value of $\Delta H_{3.1}$ calculated from the published data[25] is -124 kcal mol^{-1}. Therefore, both these reactions can yield $^3R{=}O$, whereas reaction (3.1) can produce also $^1R{=}O$ ($E_T = 68.6$, $E_S = 83.7$ kcal mol^{-1}).[13]

With the aim of identifying the stage of chemiexcitation, let us consider the dependence of I_0 on $[RN_2]_0$ within the framework of the suggested mechanism.

According to Scheme 1, the intensity of chemiluminescence is described by the following equation:

$$I = \Phi_{40} \cdot k_{40}[{}^3R{=}O],$$

where Φ_{40} is the quantum yield of radiation.

The stage of chemiluminescence is described by reaction (3.1), whereas in the steady-state mode with $\Phi \ll 1$

$$I = \Phi_{CL}\frac{k_{40}}{k_{41}[RN_2] + k_{42}[O_2]} \cdot k_0[RN_2], \quad (6)$$

where $\Phi_{CL} = \Phi_{31}\Phi_{40}$.

When $k_{42}[O_2] \gg k_{41}[RN_2]$ and $[O_2] = [O_2]_0 = \text{const}$, from Eq. (6) we obtain

$$I = \Phi_{CL}\frac{k_{40}}{k_{42}[O_2]_0} \cdot k_0[RN_2]. \quad (7)$$

According to Eq. (7), the initial intensity of chemiluminescence I_0 is directly proportional to $[RN_2]_0$.

Equation (7) agrees well with the experimental results obtained at rather high $[O_2]_0/[RN_2]_0$ ratios (a constant concentration of oxygen in the solution was provided by suppling the reaction mixture with gas).

Let us consider the situation, when reaction (3.2) is the stage of chemiexcitation:

$$I = \Phi_{32}\Phi_{40}\frac{k_{40}}{k_{41}[RN_2] + k_{42}[O_2]} \cdot 2k_{32}(k_0/k_{31})^2.$$

In this case, one would expect that the value of I_0 will decrease with increasing $[RN_2]_0$, which is contradictory to the experimental results.

Therefore, reaction (3.2) does not contribute significantly to generation of $^3R{=}O$. This conclusion is true also for any other potentially possible reaction of chemiexcitation, which does not involve RN_2 as a reagent.

Equation (7) can be used for determining the rate constant of overall decomposition of $[RN_2]$:

$$I = F[RN_2]_0 e^{-k_{RN_2}t},\ \ln(I_0/I) = k_{RN_2}t, \quad (8)$$

here

$$F = \frac{\Phi_{CL}k_0k_{40}}{k_{42}[O_2]_0}.$$

Determination of k_0. By comparing Eqs. (1), (4), and (5) and Eqs. (2) and (8), we obtain

$$k_{sp} = k_{CL} = k_{RN_2} \approx 2k_0. \quad (9)$$

Using the experimental values of k_{sp} and k_{CL} (in the overall range of changes in the $[RN_2]_0/[O_2]_0$ ratio by a factor of 150), we can calculate

$$k_0 = (1.3\pm0.1) \cdot 10^{-4}\ s^{-1}.$$

According to the data reported in Ref. 26, $k_0 = 1.4 \cdot 10^{-4}$ s^{-1} (85 °C).

In conclusion, note an interesting characteristic feature of thermal decomposition of RN_2 in the presence of

O_2. The mechanism of this process involves quantum-chain reactions:

$$\dot{R}O\dot{O} \xrightarrow{RN_2} {}^3RO \xrightarrow{O_2} {}^1O_2 \xrightarrow{RN_2} \dot{R}O\dot{O},$$

$$\dot{R}O\dot{O} \xrightarrow{RN_2} {}^3RO \xrightarrow{RN_2} {}^3R \xrightarrow{O_2} \dot{R}O\dot{O}.$$

However, because of the low value of F, in each specific case the contribution of these chain reactions to the overall process is small, and these reactions may be considered only as side channels of consumption of RN_2.

We thank V. Kazakov and A. Voloshin for valuable advice and helpful discussion and E. Chainikova for determination of the solubility of oxygen.

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Received August 1, 1996