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## Abstract

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## Physical Chemistry

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# Kinetics of the Decomposition of Diazomethane in a Stream of Nitrogen

*(Presented by Academician V. N. Kondrat︠ev, April 6, 1957)*

The methylene radical $CH_2$ takes part in a number of chemical transformations; therefore the study of its reactions with molecules of various substances ($H_2$, $O_2$, $CH_4$ ...) is of considerable interest for chemical kinetics. However, since methylene itself is a decomposition product, it became necessary to study the kinetics of the decomposition of such substances as may be a source of the $CH_2$ radical. Taking into account that methylene exhibits different lifetimes depending on the conditions of its formation and on the nature of the surrounding medium ($^1$), we considered that the method of thermal decomposition of diazomethane in an inert-gas medium would make it possible to obtain $CH_2$ in its normal state and to study its reactivity.

Several papers are known in the literature in which the results of qualitative observations of the decomposition reaction of diazomethane are presented ($^{2,3}$). The authors give certain arguments in favor of a monomolecular mechanism for the primary act: $CH_2N_2 \to CH_2 + N_2$. Direct proof of the formation of $CH_2$ as the primary product of the decomposition of $CH_2N_2$ was given by the mirror method ($^4$).

## Procedure and Results

Diazomethane, obtained by decomposition of nitrosomethylurea in an alkaline medium, was dissolved in cold dibutyl phthalate, from which it was then transferred by a stream of absolutely pure nitrogen into a receiver. In this way the concentration of $CH_2N_2$ in the gas could be varied.

In preliminary experiments it was established that slow (nonexplosive) decomposition of diazomethane at high temperatures can be observed only in an inert-gas medium. It was found that, if the dilution is sufficiently great, then at corresponding values of $t^\circ$ and $\sigma$ ethylene is the only product (apart from $N_2$) of the complete decomposition of diazomethane. Unreacted diazomethane can be isolated either by low-temperature fractionation followed by complete decomposition in a stream of nitrogen, or by absorption with benzoic acid and analysis of the gaseous residue.

Table 1 gives the results of observations of the decomposition of $CH_2N_2$ in a stream of nitrogen. Column 3 gives the amount of $C_2H_4$ isolated from the reaction off-gases; column 5, the amount of ethylene obtained upon decomposition of the unreacted diazomethane. The sum of these quantities gives the $CH_2N_2$ content in the initial mixture, and their ratio gives the extent of decomposition. The last column of the table gives the values of the constants calculated according to the law for first-order reactions. From all the data it follows that the slow decomposition of diazomethane proceeds according to the equation:

$$\begin{array}{c} CH_2N_2 = N_2 + CH_2 \\ \downarrow \\ C_2H_4 \end{array} \tag{I}$$

Consequently, for this reaction under steady-state conditions the relation

$$2\Delta P = x \ldots, \tag{1}$$

must hold, where $x$ (mm) is the amount of decomposed $CH_2N_2$. Figure 1 gives the results of calculating the kinetics of diazomethane decomposition according to the law for first-order reactions, taking into account the theoretical relation (1). The good agreement of the experimental points with the calculated curve confirms the mechanism of diazomethane decomposition and the ratio of the products obtained. At higher concentrations of diazomethane in the gas mixture ($CH_2N_2 + N_2$), the calculation agrees with experiment only for the initial stage of decomposition, not complicated by secondary reactions.

**Fig. 1.** Kinetics of $CH_2N_2$ consumption under steady-state conditions in an $N_2$ medium.

## Temperature dependence of the rate of diazomethane decomposition

In the decomposition reaction of $CH_2N_2$, one may suppose the existence of secondary reactions of $CH_2$ with the original diazomethane molecule.

$$CH_2 + CH_2N_2 \rightarrow C_2H_4 + N_2. \tag{II}$$

**Table 1**

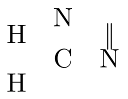
Decomposition of $CH_2N_2$ in an $N_2$ jet; $P = 20$ mm, $t = 381^\circ$

| Gas taken, mixture, l | Contact time $\theta$, sec | Found: unreacted $CH_2N_2$, $C_2H_4$ $cm^3$ | Found: unreacted $CH_2N_2$, $CH_2N_2$ $cm^3$ | Found: reacted $CH_2N_2$, $C_2H_4$ $cm^3$ | Found: reacted $CH_2N_2$, $CH_2N_2$ $cm^3$ | Concentration of $CH_2N_2$, mixture, % | Initial pressure of $CH_2N_2$, $P_0$, mm | Decomposition, % | $P_\theta$, mm | Decomposition constant, $K$, $sec^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 8.90 | 0.03 | 46.76 | 93.56 | 3.30 | 6.60 | 1.06 | 0.212 | 6.59 | 0.1981 | 2.27 |
| 4.75 | 0.52 | 9.14 | 18.28 | 20.06 | 40.12 | 1.44 | 0.288 | 68.70 | 0.090 | 2.23 |
| 4.15 | 0.49 | 3.39 | 6.78 | 7.90 | 15.80 | 0.52 | 0.104 | 72.30 | 0.029 | 2.62 |
| 2.05 | 0.14 | 7.20 | 14.40 | 3.05 | 6.10 | 1.00 | 0.200 | 29.75 | 0.141 | 2.53 |
| 3.55 | 0.08 | 17.58 | 35.16 | 3.72 | 7.44 | 1.20 | 0.240 | 17.46 | 0.198 | 2.40 |
| 4.72 | 0.53 | 11.91 | 23.82 | 26.32 | 52.65 | 1.62 | 0.324 | 68.86 | 0.101 | 2.20 |
| 4.50 | 0.50 | 4.83 | 9.66 | 12.50 | 25.00 | 0.77 | 0.154 | 72.14 | 0.043 | 2.55 |
| 6.00 | 0.35 | 13.77 | 27.54 | 19.23 | 38.46 | 1.10 | 0.220 | 58.27 | 0.092 | 2.30 |
| 4.40 | 0.50 | 6.40 | 12.80 | 15.60 | 31.20 | 1.00 | 0.200 | 70.90 | 0.057 | 2.50 |

However, the results of kinetic studies, and especially the very clear experiments with Te mirrors, show that this reaction is associated with a high activation energy or, probably, with large steric hindrances. It follows from our experiments that a relatively small increase in the decomposition temperature of $CH_2N_2$ (in the range up to 500°) sharply reduces the removal time of a standard tellurium mirror, which can be explained only by a very low probability of reaction (II) in the temperature region up to 500°. The yield of ethylene is thus the result only of recombination of methylidene radicals as the primary product of diazomethane decomposition. From the dependence $\lg K$ $(1/T)$ we find $E = 31750$ cal. The complete expression for the constant of thermal decomposition of $CH_2N_2$ will have the form:

$$K = 0.8 \cdot 10^{11} e^{-\frac{31750}{RT}}. \tag{2}$$

The value found for $E$ pertains to the process of bond redistribution in the diazomethane molecule



leading to the formation of two new particles: $CH_2 + N_2$. The value of the preexponential factor in the expression for $K$ seems quite reasonable if it is compared with the expressions for the decomposition constant of nitrous oxide, where decomposition products of similar nature are formed.

Fig. 2. Temperature dependence of the decomposition rate of $CH_2N_2$ in a nitrogen jet

Figure 1: Fig. 2. Temperature dependence of the decomposition rate of $CH_2N_2$ in a nitrogen jet

Fig. 3. Yield of $CH_2N_2$ decomposition products as a function of temperature. $C_{CH_2N_2} = 2.62\%$

Figure 2: Fig. 3. Yield of $CH_2N_2$ decomposition products as a function of temperature. $C_{CH_2N_2} = 2.62\%$

## Mechanism of diazomethane decomposition in a nitrogen jet

In studying the temperature dependence of the decomposition rate it was established that the course of the logarithmic straight line (Fig. 2) changes at $t \geq 500°$, and, as it turned out, the composition of the decomposition products also changes. Along with the main reaction product, ethylene, ethane, acetylene, and, in small amounts (1.0–1.5%), butane and propylene appear. The reaction tube becomes covered with a layer of carbon.

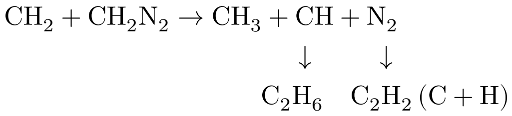
**Fig. 2.** Temperature dependence of the decomposition rate of $CH_2N_2$ in a nitrogen jet.

**Fig. 3.** Yield of $CH_2N_2$ decomposition products as a function of temperature. $C_{CH_2N_2} = 2.62\%$.

The change in hydrocarbon composition with changing temperature of $CH_2N_2$ decomposition is shown in Fig. 3. The dashed curve shows the amount of $CO_2$ obtained by burning off the carbon deposited on the walls of the reaction tube. This result, obtained by mass-spectrometric and chemical analyses, provides sufficient grounds to consider that the mechanism of thermal decomposition of diazomethane under the conditions of our experiments consists of the following sequence of transformations:

$$\begin{array}{ll}
1. & CH_2N_2 \rightarrow CH_2 + N_2. \\
2. & CH_2 + CH_2 \rightarrow C_2H_4. \\
3. & CH_2 + CH_2N_2 \rightarrow C_2H_4 + N_2. \\
4. & CH_2 + CH_2 \rightarrow \begin{array}[t]{cc} CH_3 & + \; CH \\ \downarrow & \downarrow \\ C_2H_6 & C_2H_2\,(C + H) \end{array}
\end{array}$$

4′.



$$\mathrm{CH_2 + CH_2N_2 \rightarrow \underset{\underset{C_2H_6}{\downarrow}}{CH_3} + \underset{\underset{C_2H_2\,(C+H)}{\downarrow}}{CH} + N_2}$$

5. $C_2H_6 + H \rightarrow C_2H_5 + H_2$.
6. $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$.
7. $CH_2 + C_2H_4 \rightarrow C_3H_6$.

It is obvious that the first two reactions represent the principal mode of diazomethane decomposition, occurring under all conditions. This reaction path at $t < 450°$ in an inert-gas medium is the only one, which may apparently be regarded as fully proven. At $t \geq 500°$, the possibility arises of secondary reactions of the methylene radical. Of these, the significance of reactions 5, 6, and 7 is small. The overall maximum yield of higher hydrocarbons ($\Sigma C_3 + C_4$) exceeds 1.5%.

Of special interest is the mechanism of ethane formation. It is clear, however, that its appearance among the decomposition products can be explained in only two ways: either by the disproportionation reaction of methylene radicals (4), or by their interaction with the initial diazomethane molecule (4′).

It is impossible to provide convincing evidence in favor of the exclusive selection of one of them, or of the share of their joint participation. Completely analogous conditions also arise in the decomposition reaction of ketene. Thus, from the temperature dependence of the yield of ethane (at $t > 500°$) in the decomposition of diazomethane or ketene, it is not possible to determine the value of the activation energy for the disproportionation reaction of methylene radicals. From the course of the accumulation curves of $C_2H_6$ and $C_2H_4$ (Fig. 3) one may only suppose that this value should be of the order of 18–20 kcal.

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