# The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites. II. The Decomposition of Ethyl Nitrite

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The thermal decomposition of gaseous ethyl nitrite is a homogeneous first order reaction. It proceeds at a conveniently measurable rate between 190 and 240°C. The overall reaction is mainly

$$C_2H_5NO_2 = NO + \tfrac{1}{2}CH_3CHO + \tfrac{1}{2}C_2H_5OH.$$

The rate of reaction is given by

$$k = 1.39 \times 10^{14} e^{-37,700/RT} \text{ sec.}^{-1}$$

There is no falling off in rate down to 5 cm pressure. On account of their similarity and simplicity the comparison of the decompositions of methyl and ethyl nitrite is of considerable interest. Further work is in progress on the propyl and butyl nitrites.

## Introduction

IT is of considerable interest to investigate the homogeneous unimolecular decomposition of a series of related chemical compounds. The only series so far investigated is that of the aliphatic ethers.[1] The ether decompositions, however, are complicated, and in consequence it is difficult to make comparisons between them. It has recently been shown[2] that the decomposition of methyl nitrite is a homogeneous first order reaction. The decomposition is simple, the rate determining step being apparently the splitting off of nitric oxide, and hence it is of interest to investigate the decomposition of other alkyl nitrites. The present paper deals with ethyl nitrite.

## Experimental

Reaction velocities were measured as before by observing the rate of pressure change in a system at constant volume. The reaction vessels were Pyrex bulbs having a capacity of about 125 cc. The apparatus was similar to that used in a number of previous investigations.[3] The required temperatures were obtained by the use of a well stirred oil bath, heated electrically. Temperatures were measured with standard mercury thermometers. The temperature could be maintained constant to within 0.25°C.

Ethyl nitrite was prepared by the addition of a solution of nitrous acid to ethyl alcohol. The gas evolved was purified by passing it through a 50 percent sodium hydroxide solution, followed by a 40 percent ferrous sulphate solution to remove nitrogen oxides. It was then roughly dried by passage over calcium chloride. The gas was then condensed and fractionally distilled twice. During the course of the investigation the ethyl nitrite was stored as a liquid in a cooled bulb.

## Experimental Results

### The products of the reaction

Since the form of the reaction rate curves and the total pressure increase at completion did not vary with temperature or pressure, as will be shown later, it follows that there cannot be much variation in the products of reaction with varying conditions.

[1] Hinshelwood and co-workers, Proc. Roy. Soc. **A114**, 84 (1927), **A115**, 215 (1927), J. Chem. Soc. **1929**, 1804. Steacie, J. Phys. Chem. **36**, 1562 (1932), J. Chem. Phys. **1**, 313, 618 (1933). Kassel, J. A. C. S. **54**, 3641 (1932). Ure, J. Phys. Chem. **37**, 1169, 1183 (1933).

[2] Steacie and Shaw, Proc. Roy. Soc. (London), in press.

[3] Steacie, Can. J. Research **6**, 265 (1932).

Some typical analyses of the gaseous products at completion follow:

| | | |
|---|---|---|
| NO, % | 94.2 | 88.0 |
| CO, % | 1.3 | 3.3 |
| Residue, % | 4.5 | 8.7 |

In the above analyses NO was determined by absorption with slightly acidified ferrous sulphate. Gas analysis in the presence of nitrogen oxides is necessarily difficult, and in view of this fact the above results are in satisfactory agreement. The gaseous products are very similar to those of the methyl nitrite decomposition, the average values for methyl nitrite being NO = 84 percent, CO = 7 percent, residue = 9 percent.

The condensable products of the reaction were determined by means of experiments in a special reaction vessel, so constructed that it could be washed out with water after each run. The washings gave a pronounced Schiff test for aldehydes. If the solution were warmed up to distill off aldehydes, and sulphuric acid added, a positive Schiff test was again obtained, pointing to the presence of alcohols which had been oxidized to aldehydes. By analogy with the methyl nitrite decomposition it may therefore be concluded that the condensable products consist of acetaldehyde and ethyl alcohol. This is supported by the fact that the condensable products were liquids, that ethyl alcohol could be detected by its odor, and that there was no sign of a deposit of paraformaldehyde.

We may therefore conclude that the reaction proceeds in a manner similar to that of methyl nitrite, *viz.*,

$$C_2H_5NO_2 = NO + \tfrac{1}{2}C_2H_5OH + \tfrac{1}{2}CH_3CHO.$$

This mechanism was confirmed by a determination of the relative amounts of liquid and gaseous products. A run was made at 235°C with an initial pressure of 27.0 cm. At completion the pressure was 51.5 cm, an increase of 24.5 cm. The reaction vessel was then cooled to −80°C. At this temperature the pressure was 9.98 cm. Calculating the pressure which this amount of gas would exert at 235°C, we obtain 26.3 cm. This is almost exactly equal to the initial pressure of ethyl nitrite. Hence, in agreement with the above mechanism, we obtain 1 molecule of non-condensable material from each molecule of ethyl nitrite. The reaction vessel was then heated

to 13°C, and the pressure was found to be 23.6 cm. The calculated NO pressure at 13°C is 14.8 cm. At 13°C the vapor pressure of ethyl alcohol is 2.4 cm. Acetaldehyde should all be in the gas phase at this temperature. If we assume all the gas other than NO and alcohol vapor to be acetaldehyde, then the partial pressure of acetaldehyde at 13°C is 6.4 cm. This is somewhat less than half the NO as required by the above mechanism. However, considering the small amount of alcohol present, it is doubtful if vapor pressure equilibrium would really be reached, and hence the amount of acetaldehyde present is probably larger than that calculated. Finally, it was shown that all the products were gaseous at 87°C, as would be the case if ethyl alcohol were the remaining product.

It may therefore be concluded that the overall reaction is the one given previously. The mechanism is presumably the following:

$$C_2H_5NO_2 = C_2H_5O + NO \qquad (1)$$

$$C_2H_5O = CH_3CHO + H \qquad (2)$$

$$H + C_2H_5O = C_2H_5OH. \qquad (3)$$
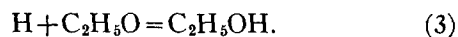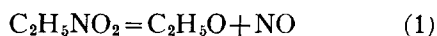
This is consistent with the work of Rice[4] and his collaborators on free radicals in the decomposition of organic compounds.

### The pressure change accompanying the reaction

The mechanism given above would lead to a pressure increase of 100 percent at completion. Actually the observed pressure increases average about 86 percent. Some typical values are given in Table I.

TABLE I. *Maximum pressure increases.*

| Temperature (°C) | Initial pressure (cm) | | Maximum pressure increase (percent) |
|---|---|---|---|
| 199.9 | 23.89 | | 88.7 |
| 209.8 | 13.48 | | 90.3 |
| 209.8 | 18.48 | | 83.3 |
| 219.9 | 28.40 | | 90.7 |
| 219.9 | 33.36 | | 83.3 |
| 230.2 | 22.85 | | 84.2 |
| 230.2 | 23.21 | | 85.3 |
| 240.7 | 27.96 | | 80.7 |
| | | Mean | 85.8 |

[4] Rice *et al.*, J. A. C. S. **53**, 1959 (1931); **55**, 3035 (1933); **56**, 284 (1934).

If we assume that 86 percent pressure increase corresponds to complete reaction, then $T_{25}$ and $T_{50}$ (the times for the pressure to increase 25 and 50 percent, respectively) correspond to 29.1 and 58.2 percent reaction. Theoretically therefore $T_{50}/T_{25}$ should be equal to 2.54 if the reaction is first order. Actually the mean ratio for all runs is 2.57. It therefore seems to be justifiable to use the values of $T_{25}$ and $T_{50}$ as a measure of the rate of reaction, and to assume that they correspond to 29.1 and 58.2 percent reaction, respectively.

## The rate of reaction

Complete data for some typical runs are given in Table II. It will be seen that good first order constants are obtained. The summarized data for all runs are given in Table III.

## The effect of pressure on the rate

The constancy of the values of the fractional times with varying pressure shows that the reaction is of the first order. If there is any falling off in rate at low pressures, it is of the order of magnitude of the experimental error. The reaction is under investigation at low pressures, and the results will be reported later.

TABLE II. *Data for typical runs.*

| Time (min.) | Temperature = 209.8°C Initial pressure = 36.57 cm | | | Temperature = 219.9°C Initial pressure = 20.62 cm | | |
|---|---|---|---|---|---|---|
| | $\Delta P$ (cm) | % reaction | $k$ | $\Delta P$ (cm) | % reaction | $k$ |
| 0 | 0 | 0 | — | 0 | 0 | — |
| 0.5 | 0.94 | 3.0 | 0.0257 | 1.02 | 5.8 | 0.0522 |
| 1 | 1.93 | 6.2 | 0.0274 | 2.07 | 11.6 | 0.0538 |
| 1.5 | 2.90 | 9.2 | 0.0276 | 3.09 | 17.3 | 0.0553 |
| 2 | 3.76 | 12.0 | 0.0275 | 4.08 | 23.0 | 0.0569 |
| 2.5 | — | — | — | 4.97 | 28.1 | 0.0572 |
| 3 | 5.50 | 17.5 | 0.0276 | 5.83 | 32.9 | 0.0577 |
| 4 | 7.19 | 22.9 | 0.0285 | 7.35 | 41.5 | 0.0582 |
| 5 | 8.89 | 28.3 | 0.0289 | 8.63 | 48.7 | 0.0580 |
| 6 | 10.30 | 32.7 | 0.0286 | 9.73 | 54.8 | 0.0576 |
| 7 | 11.69 | 37.2 | 0.0288 | 10.73 | 60.5 | 0.0576 |
| 10 | 15.14 | 48.2 | 0.0286 | | | |
| 14 | 19.00 | 60.5 | 0.0288 | | | |

## The effect of surface

In Table III rates are given for an empty reaction vessel, and also for a similar vessel packed with short lengths of Pyrex tubing so as to increase the surface-volume ratio to about 9 times its former value. It will be seen that there is very little difference in the rate in the two vessels. It may therefore be concluded that if any heterogeneous reaction occurs in the empty bulb, it constitutes less than one percent of the whole process.

TABLE III. *The rate of reaction.*

| Reaction vessel | Temperature (°C) | Initial pressure (cm) | $T_{12.5}$ (sec.) | $T_{25}$ (sec.) | $T_{50}$ (sec.) | Reaction vessel | Temperature (°C) | Initial pressure (cm) | $T_{12.5}$ (sec.) | $T_{25}$ (sec.) | $T_{50}$ (sec.) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Empty | 189.9 | 32.68 | 828 | 1806 | 4578 | Empty | 219.9 | 33.36 | 66.0 | 152 | 387 |
| " | 189.9 | 36.84 | 846 | 1806 | 4518 | " | 219.9 | 37.24 | 70.8 | 137 | 338 |
| " | 189.9 | mean values | 837 | 1806 | 4548 | " | 219.9 | 44.45 | 68.4 | 145 | 369 |
| " | 199.9 | 20.74 | 378 | 798 | 1908 | " | 219.9 | 46.88 | 67.2 | 142 | 360 |
| " | 199.9 | 23.89 | 348 | 762 | 1836 | " | 219.9 | 54.50 | 66.0 | 142 | — |
| " | 199.9 | 32.95 | 328 | 716 | 1806 | " | 219.9 | mean values | 69.3 | 146.7 | 378.0 |
| " | 199.9 | mean values | 352 | 759 | 1850 | " | 230.2 | 14.44 | — | 61.8 | 154 |
| " | 209.8 | 13.48 | 156 | 323 | 846 | " | 230.2 | 23.21 | — | 64.2 | 169 |
| " | 209.8 | 21.14 | 146 | 326 | 834 | " | 230.2 | 27.48 | — | 67.2 | 174 |
| " | 209.8 | 25.17 | 141 | 307 | 744 | " | 230.2 | 30.02 | — | 63.6 | 161 |
| " | 209.8 | 26.14 | 147 | 315 | 792 | " | 230.2 | 37.48 | — | 58.8 | 157 |
| " | 209.8 | 36.57 | 150 | 310 | 792 | " | 230.2 | 38.16 | — | 57.6 | 152 |
| " | 209.8 | mean values | 148.1 | 316.2 | 802 | " | 230.2 | mean values | — | 63.3 | 166.0 |
| " | 219.9 | 5.46 | 72.0 | 157 | 432 | " | 240.7 | 18.72 | — | 29.4 | 82.2 |
| " | 219.9 | 10.26 | 72.0 | 154 | 369 | " | 240.7 | 27.96 | — | 30.6 | 81.6 |
| " | 219.9 | 13.02 | 70.8 | 134 | 371 | " | 240.7 | mean values | — | 30.0 | 81.9 |
| " | 219.9 | 13.24 | 67.8 | 144 | 387 | Packed | 209.8 | 23.93 | 136 | 280 | 786 |
| " | 219.9 | 20.62 | 75.0 | 157 | 395 | " | 209.8 | 29.78 | 126 | 267 | 780 |
| " | 219.9 | 26.34 | 73.8 | 154 | 384 | " | 219.9 | 23.35 | 64.2 | 145 | 366 |
| " | 219.9 | 28.40 | 67.8 | 144 | 364 | " | 219.9 | 27.72 | 66.6 | 144 | 382 |
| " | 219.9 | 32.87 | 66.0 | 132 | 360 | " | 230.2 | 22.85 | — | 61.8 | 164 |
| " | 219.9 | 33.29 | 67.8 | 148 | 379 | " | 230.2 | 33.38 | — | 66.6 | 168 |
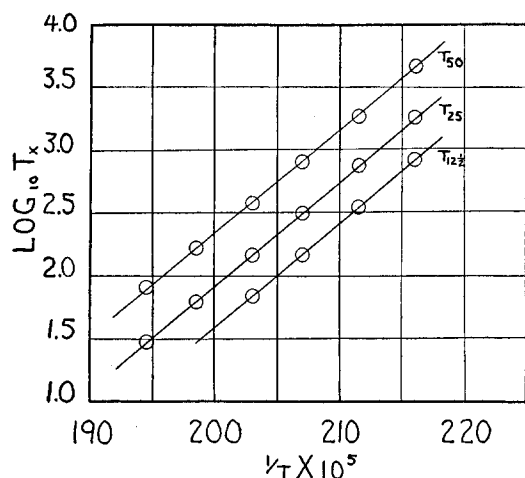
FIG. 1. The temperature coefficient.

## The temperature coefficient

In Fig. 1 the logarithms of the fractional times are plotted against the reciprocal of the absolute temperature. The data used are the mean values given in Table III. From the slopes of the lines we obtain the following values for the heat of activation:

| | |
|---|---|
| From $T_{12.5}$ | 38,100 calories per gram molecule |
| From $T_{25}$ | 37,550 |
| From $T_{50}$ | 37,550 |
| Mean | 37,700 |

The rate of reaction may therefore be expressed by

$$T_{25} = 2.47 \times 10^{-15} e^{37,700/RT} \text{ sec.}$$

Or, since $T_{25}$ represents 29.1 percent reaction,

$$k = 1.39 \times 10^{14} e^{-37,700/RT} \text{ sec.}^{-1}.$$

## DISCUSSION

The comparison of the decomposition of ethyl and methyl nitrites is of some interest. Both reactions are extremely simple unimolecular changes in that they presumably involve the direct splitting of only one bond, i.e.,

$$CH_3 - O - NO = CH_3O + NO$$

$$C_2H_5 - O - NO = C_2H_5O + NO.$$
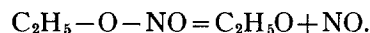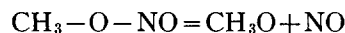
The activation energies for both reactions are about 37,000 calories. The energy available to break the bond is therefore (37,700 cal.+average energy of the molecules). The number of degrees of freedom involved is at least 12, and is probably much greater. If we assume $n = 12$ and $n = 20$, then we have available at 500°K, 43,000 and 47,000 calories, respectively. There are no direct estimates available of the energy required to split the $-O-NO$ bond. Rice and Johnston[5] found approximately 80,000 calories for $C-O$, 70,000 to 80,000 for $C-C$, and about 50,000 for $C-N$. It therefore seems probable that the energy available here is sufficient to break the $O-NO$ bond. Hence if the reaction in this case proceeds through a free radical mechanism[6] it is not necessary to assume the existence of reaction chains.

The discussion of the effect of chemical configuration on the activation energy, etc., will be deferred until data are available for the propyl and butyl nitrites.

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[5] Rice and Johnston, J. A. C. S. 56, 214 (1934).
[6] Rice and Herzfeld, J. A. C. S. 56, 284 (1934).