

The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites VIII. The Decomposition of Ethyl and nPropyl Nitrites at Low Pressures Together with a General Discussion of the Results for the Entire Series

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The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites

VIII. The Decomposition of Ethyl and *n*-Propyl Nitrites at Low Pressures Together with a General Discussion of the Results for the Entire Series

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The kinetics of the decomposition of ethyl and *n*-propyl nitrites have been investigated at low pressures. The results, together with those for the other members of the nitrite series, are discussed from the point of view of the Kassel theory. Attention is focused particularly on the effect of increasing molecular complexity as one ascends an homologous series, since the nitrites furnish an ideal series for such a discussion. It is concluded that the Kassel

theory furnishes a complete explanation of the facts insofar as the effect of pressure on the rate is concerned. On the other hand, there is no satisfactory quantitative explanation of the increase in the high pressure rate with increasing molecular complexity. The factors which might contribute to such an increase are discussed, and it is concluded that the main factor is probably a progressive change in binding energy as one ascends an homologous series.

INTRODUCTION

CONSIDERABLE attention has been directed in recent years to the study of unimolecular reactions. It now appears that the initial step in nearly all organic decompositions is unimolecular in character, and that the whole question of the stability of gaseous organic substances is virtually reduced to the determination of the unimolecular rate constants.

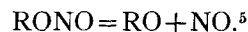
The variation of the constants *A* and *E* in the expression for the rate constant,

$$k = Ae^{-E/RT},$$

as one passes from one member to the next in an homologous series has been the subject of frequent investigation during the past few years. In general a number of criticisms may be directed against the series of compounds previously investigated. In the case of the aliphatic ethers the mode of decomposition varies from member to member of the series, and in any case recent work seems to indicate that the decompositions are much more complex than appeared at first sight.¹ The azo compounds² in addition to possessing a somewhat complex decomposition mechanism, are further complicated by the presence of a side reaction of increasing prominence as one goes up the series. The esters and

paraldehydes³ are rather more satisfactory for comparative purposes. Here, too, however, while the reactions are definitely comparable, they involve a mechanism in which two bonds are broken and one other bond is converted from single to double. The physical significance of the energy of activation is therefore somewhat obscured.

Recently a series of investigations on the decomposition of the gaseous alkyl nitrites has been made in this laboratory.⁴ It appears that the primary and rate determining step in all cases is



Hence only one bond is broken in the reaction, and it is the same bond for every member of the series. The reactions have also been shown to be homogeneous and unimolecular over a wide pressure range.

The present communication deals with an investigation of the decomposition of ethyl and *n*-propyl nitrites at low pressures, together with a general discussion of the results for the entire series.

³ Coffin, *Can. J. Research* **5**, 636 (1931); **6**, 417 (1932); **7**, 75 (1932); **9**, 603 (1933).

⁴ Steacie and Shaw, *J. Chem. Phys.* **2**, 345 (1934); **3**, 344 (1935); *Proc. Roy. Soc. (London)* **A146**, 388 (1934); **A151**, 685 (1935); Steacie and Calder, *J. Chem. Phys.* **4**, 96 (1936); Steacie and Rosenberg, *ibid.* **4**, 223 (1936); Steacie and Smith, *ibid.* **4**, 504 (1936).

⁵ Rice and Rodowskas, *J. Am. Chem. Soc.* **57**, 350 (1935).

¹ Rice and Sickman, *J. Am. Chem. Soc.* **56**, 1444 (1934); Steacie and Solomon, *J. Chem. Phys.* **2**, 503 (1934); Steacie, Hatcher and Rosenberg, *ibid.* **4**, 220 (1936).

² Ramsperger, *J. Am. Chem. Soc.* **49**, 912, 1495 (1927); **50**, 714 (1928); **51**, 2134 (1929).

EXPERIMENTAL

Ethyl nitrite was prepared and purified under reduced pressure as previously described. It was stored as a liquid in a bulb at -80°C during the investigation.

The reaction was carried out in a constant volume system, and was followed by observing changes in pressure. The reaction vessels were two Pyrex bulbs of about one liter capacity. One of them possessed a surface volume ratio of about 0.6 cm^{-1} ; the other was packed with short lengths of Pyrex tubing, giving a surface volume ratio of about 3.0 cm^{-1} . The reaction vessel was immersed in an electrically heated oil bath, the temperature of which could be maintained constant to within 0.2° by manual control. Temperatures were measured by means of standard mercury thermometers.

In the higher pressure range the apparatus was constructed of 3/16-inch tubing, with stopcock connections lubricated with Apiezon N grease. Pressure changes were followed with a differential mercury manometer, and readings could be taken at very frequent intervals. (See Table I.) At lower pressures wider tubing was employed, all stopcocks were replaced by mercury seals, and a set of McLeod gauges was substituted for the manometer. These gauges

TABLE I. Complete data for typical runs with ethyl nitrite. Run No. 9. 494.6°K . Initial pressure = 10.9 cm. Pressure measurements made with a manometer.

Time (sec.)	ΔP (cm)	k (sec. $^{-1}$)	Time (sec.)	ΔP (cm)	k (sec. $^{-1}$)
0	0.0	—	300	5.2	0.0029
15	0.3	0.0023	360	5.7	0.0028
30	0.6	0.0025	420	6.15	0.0028
45	1.0	0.0026	480	6.6	0.0028
60	1.35	0.0028	600	7.2	0.0028
90	2.0	0.0029	840	8.0	0.0028
120	2.65	0.0028	1500	8.65	0.0024
180	3.60	0.0029	2100	8.85	0.0025
240	4.5	0.0029	3000	8.9	—

Graphically $T_{25} = 102\text{ sec.}$, $T_{50} = 235\text{ sec.}$

Run No. 84. 494.6°K . Initial pressure = 0.0422 cm. Pressure measurements made with a McLeod gauge.

Time (sec.)	ΔP (cm)	k (sec. $^{-1}$)	Time (sec.)	ΔP (cm)	k (sec. $^{-1}$)
0	0.0	—	1800	0.0304	0.00131
300	0.0130	0.00142	2400	0.0376	—
600	0.0210	0.00136	3000	0.0376	—
900	0.0269	0.00139	3600	0.0376	—
1200	0.0304	0.00138			

Graphically $T_{25} = 210\text{ sec.}$, $T_{50} = 510\text{ sec.}$

were of very small volume to reduce to a minimum dead space fluctuations when they were cut in and out of the system. Actually each gauge comprised less than one percent of the total volume of the reacting system and about ten percent of the total dead space.

A number of control runs were made to check the time necessary for the establishment of pressure equilibrium, etc. The system could be consistently evacuated to about 10^{-5} cm by means of a two-stage steel Leybold diffusion pump, and no appreciable pressure change occurred when the system was cut off from the pump and allowed to stand for a time comparable with the duration of a normal experiment. On a few occasions the system was flushed out with nitrogen before making a run, but this procedure had no effect upon the result. During a number of runs a piece of gold foil was inserted between the reaction vessel and the mercury surfaces of the gauge and cutoff, but this also had no observable effect on the progress of the reaction. It was also shown that heating the gauges and connecting tubing to 90°C during runs had no effect on the rate of reaction or upon the pressure increase at completion. Various samples of ethyl nitrite were used, and these gave identical results.

In carrying out an experiment the reaction system was first cut off from the pump. A suitable amount of ethyl nitrite vapor was then expanded into the reaction system by opening the stopcock or mercury cutoff leading to the reservoir for seven seconds. The initial pressure reading was made eight seconds later, and further readings were taken at intervals until the pressure ceased to change. In runs made with a McLeod gauge, the gauge was kept connected to the reaction system between observations, and was cut off only when readings were being taken. It was, of course, impossible to make readings as frequently with a McLeod gauge as with a manometer.

Propyl nitrite was prepared and stored in a manner analogous to that of ethyl nitrite. Several samples were prepared at normal and at reduced pressures, and their purity was checked by boiling point determinations. All runs were made at pressures below 3 cm, using McLeod gauges. To eliminate the possibility of the condensation of the products of reaction, all experi-

ments were made with the gauges thermostated at 100°C and with the connecting tubing heated electrically to the same temperature. Runs made with the packed reaction vessel did not deviate appreciably from those with the empty vessel. In spite of all precautions, the experiments with propyl nitrite were much less reproducible than those with ethyl nitrite. There seemed to be no apparent explanation of this fact.

EXPERIMENTAL RESULTS

All runs were carried to completion. The times for 50 percent, and 25 percent, of the total pressure increase to occur were obtained graphically, and were used as a measure of the rate of reaction.

I. Ethyl nitrite

In all about 100 runs were made at three different temperatures. Complete data for two runs in the empty reaction vessel are given in Table I. The data for all runs are given in Figs. 1 and 2, in the form of $\log P - \log 10^4/T_{50}$ and $\log P - \log 10^4/T_{25}$ graphs, and the data for a series of representative runs are given in Table II.

The mean pressure increase for all runs was 84.8 percent, in excellent agreement with Steacie and Shaw's high pressure value of 86 percent. The final pressure was quite sharply defined, and showed no tendency to fall off slowly as was reported in the case of methyl nitrite.

For the sake of comparison, Steacie and Shaw's high pressure rates are plotted in Fig. 1 (indicated by double circles). The agreement is remarkably good. It may be observed that Steacie and Calder reported rates slightly lower than those of Steacie and Shaw in the case of methyl nitrite, and this is also the case here at the one temperature at which the difference was appreciable.

Runs made with the packed reaction vessel are indicated by solid circles in Fig. 1. It is obvious that the reaction is not appreciably heterogeneous down to pressures of 10^{-2} cm.

II. *n*-Propyl nitrite

The experiments with propyl nitrite were all made at 483.6°K. Considerable difficulty was experienced in obtaining reproducible data, and,

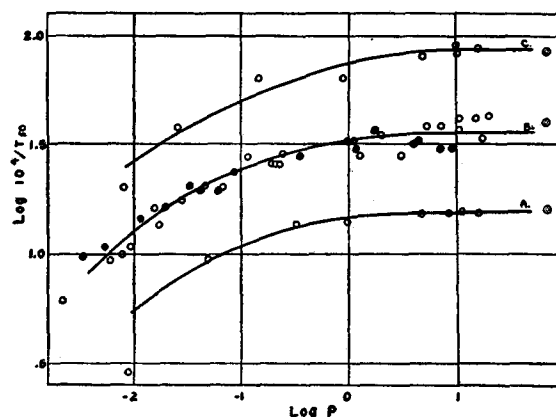


FIG. 1. The variation of T_{50} with pressure for ethyl nitrite.

as Table III and Fig. 3 indicate, some uncertainty attaches to this work. The results are, however, accurate enough to establish fairly definitely the pressure at which the rate begins to fall off appreciably. As may be seen from Fig. 3, the agreement with the results of Steacie and Shaw is well within the experimental error. Packing the reaction vessel had no apparent effect on the results:

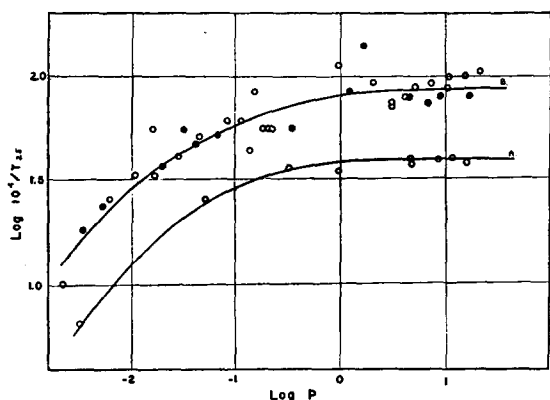
DISCUSSION

The most important characteristic of a unimolecular reaction is the falling off in rate at low pressures. As predicted by the theory, ethyl nitrite maintains its high pressure rate down to lower pressures than does methyl nitrite, and the still more complex propyl nitrite maintains it to even lower pressures.

We shall now proceed to a discussion of the effect of pressure on the rate for the alkyl nitrites from the standpoint of the Kassel theory.⁶ Kassel assumes that if a molecule has j quanta divided among s oscillators it will react when m quanta are localized in a particular bond. He then gets directly for the rate of reaction at high pressures

$$k_{\infty} = A(1 - e^{-h\nu/kT})^s \sum_{j=m}^{\infty} \binom{j+s-1}{s-1} \times \frac{j!(j-m+s-1)!}{(j-m)!(j+s-1)!} e^{-j h\nu/kT}, \quad (1)$$

⁶ Kassel, *Kinetics of Homogeneous Gas Reactions* (New York, 1932), p. 96 et seq.

FIG. 2. The variation of T_{25} with pressure for ethyl nitrite.

which, on carrying out the summation reduces to

$$k_{\infty} = Ae^{-mh\nu/kT}. \quad (2)$$

Here A has the general character of the reciprocal of a relaxation time, and ν is the frequency of the oscillators, all of which are, for simplicity, assumed to be identical.

At low pressures we must consider the number of collisions, etc., and for k , the rate at low pressures, we get

$$k = k_{\infty}(1 - e^{-h\nu/kT})^s \sum_{j=m}^{\infty} \frac{\binom{j-m+s-1}{j-m} e^{-(j-m)h\nu/kT}}{1 + \frac{A}{aN} \frac{(j-m+s-1)!j!}{(j-m)!(s-1)!}}, \quad (3)$$

where a , the collision factor, $= 4(\pi kT/m_0)^{1/2} \cdot \sigma^2$, m_0 is the molecular weight, and σ the molecular diameter.

In applying this relationship, we put $mh\nu N_0 = E$, where E is the energy of activation, and N_0 is Avogadro's number. The value of ν is adjusted so as to give agreement between the observed and calculated values of k/k_{∞} at various pressures, although, of course, it must be roughly consistent with known vibrational frequencies of the molecule. The number of effective oscillators in the molecule, s , is taken as the total number $(3n-6)$, where n is the number of atoms less the number of C-H bonds, since these possess too high a frequency to be thermally excited at the temperatures under consideration.

As a result of the series of investigations on the decomposition of the alkyl nitrites, we now

have available for the first time data for an homologous series of compounds in which (a) we are sure that exactly the same primary reaction is taking place in all cases, and (b) the substances are simple enough to enable us to determine the falling off in rate at low pressures for several members of the series.

For what we might call an ideal series of homologues, the same bond would be broken in every case, and the bond strength would be the same throughout the series. A methyl derivative possessing definite values of m and s should be followed by an ethyl derivative with $m_{et} = m_{me}$, and $s_{et} = s_{me} + 7$, and a propyl derivative with $m_{pr} = m_{me}$, and $s_{pr} = s_{me} + 14$, etc. Furthermore E , since it is equal to $N_0mh\nu$, should be constant throughout the series. Hence, from Eq. (2), k_{∞} should be the same for all members of the

TABLE II. Summarized data for representative runs with ethyl nitrite.

P_0 (cm)	Final % ΔP	T_{25} (sec.)	T_{50} (sec.)	P_0 (cm)	Final % ΔP	T_{25} (sec.)	T_{50} (sec.)
<i>Manometer 494.6°K</i>							
21.25	85.1	96	230	4.15	87.9	126	312
15.3	83.7	102	235	2.05	110.0	108	285
10.6	83.9	102	235	0.95	106.0	90	300
7.3	84.9	108	255				
<i>McLeod Gauge 494.6°K</i>							
1.12	74.2	135	300	0.0153	80.4	180	630
0.205	78.5	180	390	0.0093	89.1	420	930
0.146	74.4	120	270	0.0061	81.8	390	1080
0.0835	73.9	165	420	0.00207	86.6	1020	1650
0.0283	84.1	240	570				
<i>Packed Bulb 494.6°K</i>							
17.1	84.8	126	300	0.0332	90.3	180	480
6.9	92.1	135	330	0.00536	84.0	420	930
4.45	96.6	126	300	0.00343	84.0	540	1020
0.344	83.7	180	360				
<i>483.6°K</i>							
16.3	87.1	258	642	0.321	79.0	276	734
8.5	88.2	252	645	0.0506	72.7	390	1050
4.85	94.8	258	642	0.0032	103	1530	3510
0.996	78.9	285	720				
<i>505.0°K</i>							
15.5	86.1	—	114	0.146	70.0	—	72
4.8	82.3	—	123	0.0257	75.1	—	125
0.906	71.2	—	90	0.0083	84.3	—	228

series, provided that A does not vary. This latter probability is discussed later.

The results obtained for the high pressure rate constants of the nitrite decompositions are:

$$\begin{aligned}k_{\text{methyl}} &= 1.84 \times 10^{13} e^{-36400/RT} \text{ sec.}^{-1}, \\k_{\text{ethyl}} &= 1.39 \times 10^{14} e^{-37700/RT}, \\k_{\text{propyl}} &= 2.75 \times 10^{14} e^{-37650/RT}, \\k_{\text{iso-propyl}} &= 1.26 \times 10^{14} e^{-37000/RT}, \\k_{\text{butyl}} &= 3.02 \times 10^{14} e^{-37000/RT}.\end{aligned}$$

The variations in E are within the experimental error, but their interdependence with the non-exponential term obscures any regularities in the rates. For the moment let us arbitrarily put $E=37000$ calories per gram mole for all the reactions, and recalculate A . We get

Substance	A	A/A_m
Methyl nitrite	0.33×10^{14}	(1.0)
Ethyl nitrite	0.65×10^{14}	2.0
<i>n</i> -propyl nitrite	1.35×10^{14}	4.1
iso-propyl nitrite	1.26×10^{14}	3.8
<i>n</i> -butyl nitrite	3.02×10^{14}	9.1

In other words the rate approximately doubles for each added CH_2 group. This is in general agreement with Coffin's results. It may also be noted that within the experimental error the rates for *n*-propyl and iso-propyl nitrites are identical.

We now come to the consideration of the low pressure rates. Fig. 4 gives the experimental curve for methyl nitrite together with the predictions of the Kassel theory for $\sigma=3.0 \times 10^{-8}$ cm, $s=12$, $m=13$ and 14, and a temperature of 494.3°K . The value used for A in these calculations was one-half the experimental value, since it appears certain that in the nitrite decompositions two molecules disappear for each

TABLE III. Summarized data for experiments with propyl nitrite.
Temperature = 483.6°K .

P_0 (cm)	Final % ΔP	T_{50} (sec.)	P_0 (cm)	Final % ΔP	T_{50} (sec.)
1.066	70.5	240	0.121	77	270
0.709	68	285	0.116	78	315
0.314	72.5	360	0.0920	90	270
0.275	94	240	0.0420	83	555
0.210	66	270	0.0415	95	270
0.182	89	270	0.0395	97	360
0.125	88	270	0.0320	106	420

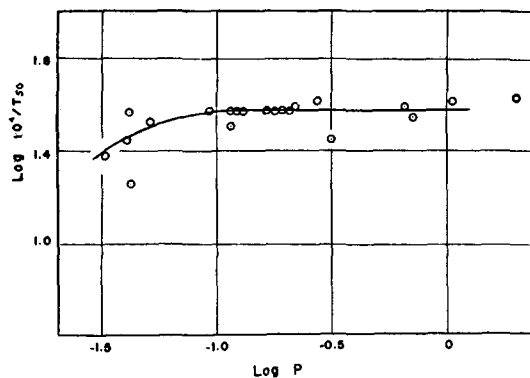


FIG. 3. The variation of T_{50} with pressure for propyl nitrite.

elementary act.⁵ The agreement of theory with experiment seems quite satisfactory with m equal to either 13 or 14.

Fig. 5 gives similar results for ethyl nitrite, s being taken as 19, and other factors as shown in the figure. It is seen that excellent agreement is obtained if we use the same values for m and σ as were used with methyl nitrite.

A similar calculation for propyl nitrite, using $s=26$ and other factors as with methyl nitrite, shows that the falling off in rate should not be appreciable above 0.1 cm. This is consistent with the experimental results given in Fig. 3.

It may therefore be concluded that the Kassel theory gives excellent agreement with the experimental facts. In this connection it should be emphasized that all adjustable parameters are exhausted in fitting the theory to the results for methyl nitrite, and that there are no further opportunities for adjustment of the theoretical values for ethyl and propyl nitrites. The nitrites, therefore, approximate very closely to the ideal homologous series discussed above. The theory, however, offers no explanation of the slight but regular increase in the high pressure rates as one ascends the series.

In looking for an explanation of this effect, it is obvious in the first place that the diameter and mass of the molecule, steric effects, etc. can have no effect since they all vanish in the expression for the high pressure rate. A variation in the proportionality factor, A , would account for the observed effect. While the significance of A is rather hazy,⁷ it has the general meaning of the

⁷ See Kassel, Chem. Rev. 10, 11 (1932).

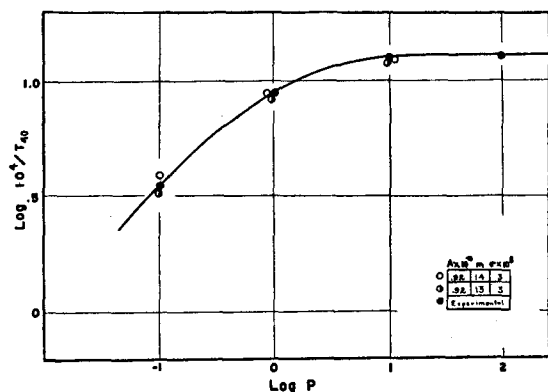


FIG. 4. Comparison of theory with experiment for methyl nitrite.

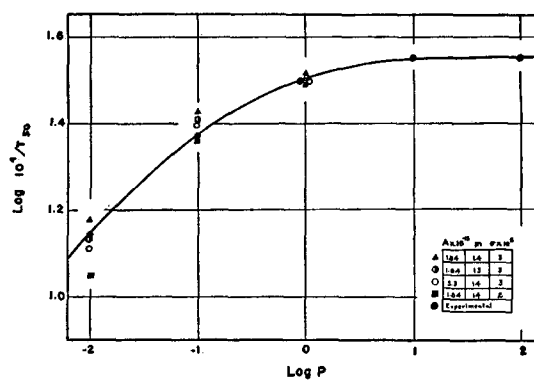


FIG. 5. Comparison of theory with experiment for ethyl nitrite.

reciprocal of a relaxation time. It would therefore be expected that it would diminish with increasing molecular complexity, which is the reverse of the experimental observations. It therefore seems unlikely that the explanation of the facts is to be found here.

There is evidence that bond strengths may diminish as we ascend an homologous series. Thus Ramsperger has reported a progressive decrease in the activation energies of the azo compounds. Rice and Johnson⁸ in discussing the strength of the C—C bond in saturated hydrocarbons report a progressive decrease in the energy of activation for the split into free radicals with increasing molecular weight. There is, of course, considerable doubt regarding the relationship between the low temperature decomposition and the free radical decomposition of the saturated hydrocarbons, but it appears almost certain that the primary step in the nitrite decompositions is a direct split into radicals, and is therefore directly comparable with Rice and Johnson's work.

It seems therefore that the most probable explanation of the increase in the high pressure rate as one ascends the nitrite series is to ascribe it to small changes in E , A probably remaining roughly constant. Since $E = N_0 m h \nu$, it follows that either m or ν must change. A change in m of 1 would correspond to a change in E of 2580 calories, while a change of 600 calories from member to member is all that is required to bring

the high pressure rates into agreement. Of course the "quanta" involved are highly artificial in character and fractional changes might be permitted. The most simple and logical assumption, however, is that there is a slight progressive decrease in ν as one ascends the series. Assuming $m = 14$ for methyl nitrite in the above calculations is equivalent to putting $h\nu = 2580$ calories per mole, whence $\nu = 910 \text{ cm}^{-1}$. All that would be required to bring the high pressure rates into line would be a decrease in ν of 15 cm^{-1} from member to member. Such a decrease is by no means unreasonable from the point of view of molecular structure.

Rice and Gershinowitz⁹ on the basis of the "freezing out" of degrees of freedom, have recently calculated the A factors for methyl and ethyl nitrites. They find the same value for both. The calculation, however, is based on the assumption of the same frequency in both cases for the bond which is about to break, and a small change in this frequency from member to member of the series could materially change the A factor.

It follows that the whole situation is complicated in that a small change in the frequency of the pertinent bond may be expected to change both A and E . At the moment there is no theory sufficiently detailed to predict accurately what will happen as one ascends an homologous series, but qualitatively at least it appears that the assumption of small changes in binding strengths is a sufficient explanation of the facts.

⁸ I. Am. Chem. Soc. **56**, 214 (1934).

⁹ J. Chem. Phys. **3**, 479 (1935).