The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites III. The Decomposition of nPropyl Nitrite

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III. The Decomposition of n-Propyl Nitrite

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The thermal decomposition of n-propyl nitrite is a homogeneous first order reaction in the temperature range 170 to 210°C. The mechanism of the decomposition is analogous to those of the other alkyl nitrites, viz.,

$$C_3H_7ONO \rightarrow NO + \tfrac{1}{2}C_2H_5CHO + \tfrac{1}{2}C_3H_7OH.$$

The rate of reaction is given by

$$K = 2.75 \times 10^{14} e^{-37650/RT} \text{ sec.}^{-1}.$$

The rates and activation energies of the various nitrite decompositions are compared. It is concluded that the increase in rate with the higher members of the homologous series is probably due to the participation of extra vibrational degrees of freedom. An estimate of the strength of the $-O-N-$ bond is made.

INTRODUCTION

THE investigation of the unimolecular decomposition of a series of chemically related compounds is of considerable interest. It has recently been shown in the first two papers of this series[1] that the alkyl nitrites constitute an ideal series of compounds from this point of view. Methyl and ethyl nitrites were shown to decompose homogeneously and unimolecularly. The decompositions are simple and appear to involve the simple splitting of the $-O-NO$ bond.

Since submitting this paper, our previous conclusions regarding the mechanism of the reaction have been completely confirmed by a paper by Rice and Radowskas.[2] By the free radical method they have shown that, as we suggested, the first step in the decomposition of ethyl nitrite is

$$C_2H_5NO_2 = C_2H_5O + NO.$$

Furthermore, their value of the activation energy for the split into radicals agrees with ours for the overall reaction, and hence confirms our conclusion that this split represents the rate determining step.

In consequence it is possible to make comparisons between the activation energies and reaction rates of the different members of the series. It is therefore desirable to investigate as many of the alkyl nitrites as possible. The present paper deals with the third straight chain member of the series, viz., n-propyl 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 previously. On account of the higher boiling point of the n-propyl nitrite and of some of the reaction products, it was necessary to heat the connecting tubing to a higher temperature than before. Stopcocks leading to the reaction vessel were therefore replaced by mercury seals, and the whole of the connecting tubing was heated during experiments to 105°C. Temperature measurement and control was as before. It was possible to keep the temperature constant to within 0.25°C.

Propyl nitrite was prepared in an analogous way to the previous nitrites, by the addition of a solution of nitrous acid to n-propyl alcohol. The liquid layer of nitrite was separated and purified by treatment with sodium carbonate solution, followed by several washings with ferrous sulphate solution to remove nitrogen oxides. It was then dried by permitting it to stand in contact with anhydrous sodium carbonate. The nitrite was then fractionally distilled and condensed twice. During the course of the investigation the n-propyl nitrite was stored in a cooled bulb.

[1] Steacie and Shaw, (I) Proc. Roy. Soc. **A146**, 388 (1934); (II) J. Chem. Phys. **2**, 345 (1934).
[2] Rice and Radowskas, J. Am. Chem. Soc. **56**, 214 (1935).

THE PRODUCTS OF THE REACTION

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

Gas analysis was carried out on the products for nitric oxide as this was shown to be the only gaseous product when the reaction bulb was cooled down to −80°C and the gas sample pumped off for analysis. Duplicate analysis gave a value of 97 percent average for NO gas present. This result is in agreement with the overall reaction given below that is advanced for the decomposition:

$$C_3H_7ONO = NO + \tfrac{1}{2}C_3H_7OH + \tfrac{1}{2}C_2H_5CHO.$$
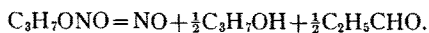
This equation requires that one molecule of NO be formed from one molecule of propyl nitrite. To confirm this, products were cooled to −80°C at which temperature the noncondensed NO gas registered the only pressure while the other products remained condensed. Instead of finding the NO pressure to be equivalent to that of the initial propyl nitrite, it was found to be invariably two-thirds. This low value is probably due to the formation of a complex between part of the NO and the condensed products at low temperatures. It may be stated here that a similar behavior was encountered in making runs where it was observed, with increasing initial pressure of propyl nitrite, there was a relative decrease in reaction rate. This difficulty was immediately overcome by raising the temperature of the cooler connecting tubing to 105°C when all runs at one temperature gave constant rates independent of the initial pressure, as will be shown later.

Thus it may be concluded from these facts and with a doubling of the pressure on completion of reaction that the decomposition of *n*-propyl nitrite is analogous to the previous nitrites investigated where the initial break is of the O − NO bond.

THE PRESSURE CHANGE ACCOMPANYING THE REACTION

The mechanism given above would lead to a pressure increase of 100 percent at completion.

TABLE I. *Maximum pressure increases.*

TEMPERATURE (°C)	INITIAL PRESSURE (cm)	MAXIMUM PRESSURE INCREASE (%)
189.9	26.68	98.4
189.9	18.34	100.0
189.9	14.68	99.2
199.9	26.52	99.2
		Mean 99.2

The pressure increases obtained were almost exactly 100 percent. Some typical values are given in Table I.

We have therefore assumed that the pressure increase is a direct measure of the reaction, and that $T_{12.5}$, T_{25} and T_{50} (the times for 12.5, 25, and 50 percent pressure increase) correspond to 12.5, 25 and 50 percent reaction, respectively. On this basis the ratio T_{50}/T_{25} should be equal to 2.44 if the reaction is first order. Actually the mean value of the ratio from all runs was 2.53.

THE RATE OF REACTION

Complete data for two typical runs are given in Table II. The first-order constants obtained

TABLE II. *Data for typical runs.*

Temperature = 210°C   Temperature = 190°C
Initial pressure = 18.38 cm   Initial pressure = 14.68 cm

TIME (min.)	ΔP (cm)	% REACTION	K	TIME (min.)	ΔP (cm)	% REACTION	K
0	0	0	—	0	0	0	—
0.5	1.50	8.2	0.172	0.5	.19	1.3	0.0257
1	2.68	14.6	0.160	1	.41	2.8	0.0272
1.5	3.54	19.3	0.145	2	.76	5.2	0.0273
2	4.33	23.6	0.136	3	1.15	7.8	0.0257
2.5	4.85	26.4	0.124	5	1.68	11.4	0.0237
3	5.36	29.1	0.119	7	2.22	15.1	0.0226
3.5	6.13	33.3	0.117	9	2.67	18.2	0.0227
4	7.11	38.6	0.124	11	3.21	21.9	0.0227
4.5	7.73	42.1	0.123	16	4.36	29.7	0.0223
5	8.28	45.1	0.122	20	5.36	36.1	0.0227
6	9.36	50.8	0.120	24	6.12	41.7	0.0228
7	10.30	56.0	0.120	32	7.53	51.2	0.0227
8	11.20	60.8	0.119	43	8.98	61.2	0.0223
9	11.96	65.0	0.118	48	9.39	64.0	0.0217
11	13.31	72.3	0.119	54	10.03	71.7	0.0216
13	14.50	78.8	0.120	60	10.53	73.8	0.0214
15	15.26	82.9	0.120	69	11.26	76.7	0.0216

are slightly high at the start, and then become very satisfactorily constant.

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. There is no indica-

tion of any falling off in rate at the lower pressures used. The investigation of the nitrite decompositions at low pressures is in progress and the results will be reported later.

THE EFFECT OF SURFACE

Experiments were made in an empty reaction vessel, and also in a vessel packed with short lengths of Pyrex tubing, so as to give an increase of about 9-fold in the surface/volume ratio. It will be seen from Table III that there was very

TABLE III. *The rate of reaction.*

(°C)	(cm)	$T_{12.5}$ (sec.)	T_{25}(sec.)	T_{50}(sec.)
		Empty bulb		
169.9	13.77	1998	4740	—
180.3	11.36	864	1980	4920
	12.50	936	2010	4572
	14.78	750	1674	4572
	19.62	792	1644	4920
	Mean	836	1827	4084
189.9	14.68	335	768	1860
	17.52	366	816	2076
	18.34	285	684	1752
	21.18	320	696	1806
	21.72	306	696	1806
	23.85	334	732	1860
	26.68	316	678	1908
	Mean	323.0	724	1860
199.9	6.08	114.0	301.8	876
	9.31	124.2	288.6	792
	16.49	124.2	312.6	762
	16.66	117.0	306.0	750
	17.67	125.4	324.0	774

(°C)	(cm)	$T_{12.5}$ (sec.)	T_{25}(sec.)	T_{50}(sec.)
		Empty bulb		
199.9	19.24	132.0	306.0	744
	26.52	148.8	326.4	756
	27.65	144.0	321.0	774
	31.24	150.0	316.2	768
	Mean	131.1	311.4	777
209.8	18.38	51.0	136.2	348.0
	22.82	58.8	145.2	360.0
	24.72	54.0	133.8	327.6
	33.88	69.0	141.0	322.4
	35.55	67.8	148.8	345.0
	Mean	60.0	141.0	342.6
		Packed bulb		
189.9	9.32	265.2	666	1620
	11.26	265.8	660	1620
	18.75	319.8	774	2100
	Mean	283.6	700	1780
199.9	13.05	122.4	297.6	762
	14.92	121.2	301.2	738
	Mean	121.8	299.4	750
209.8	16.70	57.6	136.8	360

little difference in rate in the two vessels. There is therefore no doubt that in the empty vessel there are no complications due to heterogeneity.

THE TEMPERATURE COEFFICIENT

In Fig. 1 the logarithms of the fractional times are plotted against $1/T$. The data used are the mean values given in Table III. From the slopes
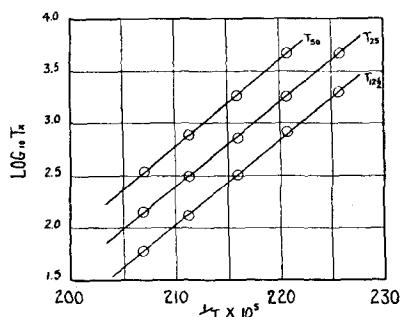

FIG. 1.

of the lines we obtain for the heat activation:

from $T_{12.5}$	37,550 calories per gram molecule
T_{25}	37,550
T_{50}	37,850
Mean	37,650

Hence the rate of reaction may be given by

$$T_{25} = 1.05 \times 10^{-15} e^{37650/RT} \text{ sec.}$$

or, since $KT_{25} = 0.288$,

$$K = 2.75 \times 10^{14} e^{-37650/RT} \text{ sec.}^{-1}.$$

DISCUSSION

In the past attempts have been made to compare the unimolecular decompositions of series of related compounds. In most cases, however, such attempts have not been very successful on account of complications, such as side reactions, which make the decompositions of the different members of a series not strictly comparable. In addition, in most cases previously investigated two or more chemical bonds are being broken in the overall reaction process, and this makes the actual elementary reaction very uncertain.

In the present case, there seems to be no doubt that all the nitrite decompositions so far investigated are directly comparable, and that in each case the primary reaction involves the rupture of only one chemical bond. The nitrites therefore furnish an ideal series for purposes of comparison. Obviously such a comparison can be more accurately made when measurement at low pressures have been completed, and when data are available for higher members of the series. It seems, however, to be worth while to make a qualitative comparison of the results so far obtained.

The rates of the three decompositions are given by an equation of the form

$$K = A e^{-E/RT}, viz:$$

Methyl Nitrite	$K = 1.84 \times 10^{13} e^{-36400/RT}$ sec.$^{-1}$,
Ethyl Nitrite	$K = 1.39 \times 10^{14} e^{-37700/RT}$ sec.$^{-1}$,
n-Propyl Nitrite	$K = 2.75 \times 10^{14} e^{-37650/RT}$ sec.$^{-1}$.

The chief difficulty in making comparisons is that the exponential and nonexponential factors in the rate expression are interdependent. As a result experimental errors cause fluctuations in

the two which are much greater than the error in determining the absolute rate. It is therefore advisable perhaps, first of all to compare the velocity constants at some definite temperature. At 189.9°C we have

Methyl	$K = 0.97 \times 10^{-4}$ sec.$^{-1}$,
Ethyl	$K = 1.89 \times 10^{-4}$ sec.$^{-1}$,
Propyl	$K = 3.95 \times 10^{-4}$ sec.$^{-1}$.

Whence we have

$$K_{Me} : K_{Et} : K_{Pr} = 1 : 1.95 : 4.07.$$

In other words the rate is almost exactly doubled on going from one member to the next. This is also equivalent to stating that, if we assume that the variations in E are due to experimental error, then A is approximately doubled as we go from one member of the series to the next. It seems, however, very unlikely that E should remain constant while A varies in this way, since the variation in the collision number will be comparatively small. In any case, however, there is no doubt that E changes only very slightly as we go up the series.

The Constancy of Two Dipole Moments in the Vapor State and Their Apparent Variation in Solution

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The validity of the solution method for the determination of dipole moment is considered with particular reference to the possible variation of moment with temperature. The moments of heptyl bromide and butyl chloride in the vapor state are found to be 2.07 ± 0.05 and 2.04 ± 0.01, respectively, which show the absence of appreciable increase in moment in the normal alkyl chlorides and bromides with increase in the length of the carbon chain beyond ethyl. Consideration of these values together with data for the alkyl halides in solution leads to the following estimated moment values for the vapor state: *n*-propyl bromide and *n*-butyl bromide, 2.04 ± 0.03; *n*-propyl iodide and *n*-butyl iodide, 1.93 ± 0.04.

THESE measurements in the vapor state were made for the sake of careful comparison with previous measurements in solution upon two substances which apparently showed abnormally and improbably high values of the atomic polarization. The comparison takes on added interest now because of recent work on the effect of solvent upon the apparent value of a dipole moment determined in solution.

Because of the rise of the apparent value of the dipole moment determined in solution with rising temperature, Jenkins[1] has stated that measurements in solution cannot be used for studying the variation of the real moment with temperature. Obviously, a small variation of the apparent moment in solution with rising temperature is not to be taken as evidence of variation in the real moment of the molecule, nor has it been generally so regarded. Many apparent

small rises in moment from 25° to 50° in solution[2] have not been treated as significant. An abnormally large rise, however, in the case of diethyl succinate led to further investigation[3] which established the reality of the effect along with the rise of moment with temperature in ethylene chloride and chlorobromide. At the same time, an apparent smaller rise for ethyl acetate was disregarded.

Obviously, as the real variation of moment with temperature depends upon the potential energy between the movable parts containing the dipoles, the presence of a solvent around the molecule may be expected to affect the effective value of the moment as well as its variation. Thus, the moments found for ethylene chloride,

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[1] H. O. Jenkins, Trans. Faraday Soc. **30**, 739 (1934).

[2] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **53**, 527, 2115 (1931); ibid. **54**, 1854, 3230 (1932).

[3] C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr., J. Am. Chem. Soc. **53**, 4242 (1931).