The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites VI. The Decomposition of nButyl Nitrite

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The figures in Table IV, suggest that the efficiency of gases in acting as third bodies in the recombination process is smaller in the case of monatomic gases, and greater in that of the diatomic and polyatomic ones—obviously because the additional degrees of freedom make an energy transfer from the atom pair to the molecule an easier one. In the group of monatomic gases, as well as in that of the polyatomic ones, the efficiency generally increases with increasing size of the molecules (or with increasing intensity of van der Waals forces).[10] A more detailed discussion of this point will be attempted on a later occasion, in connection with the results obtained in an analogous investigation with bromine.[11]

Our heartiest thanks are due to Professor F. G. Donnan, F.R.S., for the possibility he gave us to work in the Sir William Ramsay Laboratories and for his kind interest in our work.

[10] It is possible that the greater influence of O_2 as compared to that of N_2 is due to the magnetic interaction of the oxygen molecule with the iodine atoms.
[11] Communicated in Trans. Faraday Soc. 32, 907 (1936).

The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites

VI. The Decomposition of n-Butyl Nitrite

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The decomposition of n-butyl nitrite has been investigated from 5 to 40 cm pressure in the temperature range 170 to 212°C. The reaction is homogeneous and first order. The mechanism is, in the main, the same as with the lower members of the series. The reaction is, however, complicated by the formation of condensation products and the results are therefore less accurate than those obtained with the lower members of the series. The activation energy is approximately the same as those of the other nitrites. The velocity constant at 189.9°C is 8.88×10^{-4} sec.$^{-1}$, as compared with 0.97 for methyl, 1.89 for ethyl, and 3.95 for n-propyl nitrite.

INTRODUCTION

IN a number of previous papers it has been shown that the thermal decompositions of the gaseous alkyl nitrites are homogeneous unimolecular reactions. All the lower members of the series appear to decompose primarily by splitting off nitric oxide and forming a free radical, *viz.*

$$RONO = RO + NO.$$
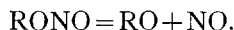
In consequence the activation energies, etc., are directly comparable for the various members of the series, and the reactions furnish an ideal opportunity to investigate the effect of chemical configuration on the reaction rate. The decompositions of methyl,[1] ethyl,[2] n-propyl,[3] and isopropyl[4] nitrites have already been investigated, and the present communication describes the decomposition of the next straight-chain member of the series, n-butyl nitrite.

EXPERIMENTAL

As before reaction rates were measured by observing the rate of pressure change in a system at constant volume. On account of the higher boiling point of n-butyl nitrite, however,

[1] Steacie and Shaw, Proc. Roy. Soc. (London) A146, 388 (1934); Steacie and Calder, J. Chem. Phys. 4, 96 (1936); Steacie and Rosenberg, ibid. 4, 223 (1936).
[2] Steacie and Shaw, J. Chem. Phys. 2, 345 (1934); Rice and Radowskas, J. Am. Chem. Soc. 56, 214 (1935).
[3] Steacie and Shaw, J. Chem. Phys. 3, 344 (1935).
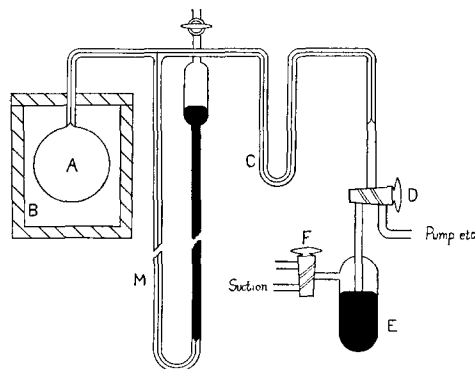[4] Steacie and Shaw, Proc. Roy. Soc. (London) A151, 685 (1935).

FIG. 1. Apparatus.

some modification of the apparatus previously employed was necessary. The modified portion of the apparatus is illustrated in Fig. 1.

The soft glass reaction vessel A, having a capacity of about 200 cc, was immersed in a well-stirred oil-bath. The temperature was determined with a thermocouple and with standard mercury thermometers. The reaction vessel was connected to a capillary manometer M, and through the U-tube C and the stopcock D to the pumps, nitrite supply, McLeod gauge, etc. All the connecting tubing except the bottom half of the U-tube and the last few centimeters before the tap D was wound with nichrome wire and heated electrically to about 115–125°C.

Prior to making an experiment, the reaction vessel was brought to the desired temperature, and the apparatus was evacuated through stopcock D by means of a diffusion pump. The bottom part of the U-tube C was then cooled with liquid air, and a roughly measured quantity of butyl nitrite was condensed into the U-tube. The two-way stopcock D was then turned so as to connect the reaction system to the trap E. By opening the tap F to the atmosphere mercury was forced through D and up the tube beyond D for a distance of 10 or 15 cm, and D was then closed. As a result D was completely isolated from the reaction system, and all the connecting tubing could be heated. The liquid air container was then removed from C, and, after a preliminary warming to −80° with solid carbon dioxide, the U-tube was surrounded with a small oil-bath heated to 125°C. The butyl nitrite in C evaporated almost instantaneously, and registered its pressure on the manometer M. The rate of the decomposition was then followed by observing the rate of pressure change in the usual way.

n-butyl nitrite was obtained from the Eastman Kodak Company. It was carefully fractionated, and the fraction boiling at 76–77.8°C was retained.

THE COURSE OF THE REACTION

Inasmuch as the activation energy and the absolute rate of the decomposition were similar to those of the other nitrites, there seems to be little doubt that, as before, the primary step is the rupture of the O − NO bond,
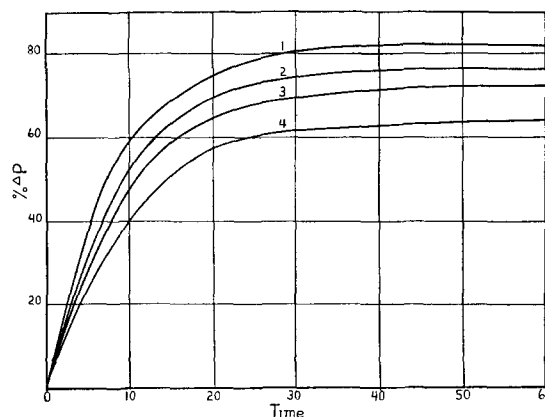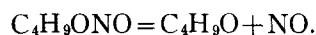
$$C_4H_9ONO = C_4H_9O + NO.$$

Fig. 2. Pressure increase-time curves.
Temp. = 201.8°. 1—25.6 cm; 2—18.2; 3—13.4; 4—9.5.

This would, by analogy, probably be followed by reactions leading to butyl alcohol and butyraldehyde. However, the course of the reaction was by no means as smooth as with the lower members of the series, and considerable amounts of carbon and tarry materials were deposited in the reaction bulb and connecting tubing. In view of the difficulties of analysis of such mixtures of products, and of the fact that the internal evidence completely supports the conclusion that the primary reaction is as before, no attempt has been made to determine the products of the reaction.

In previous investigations the pressure increase at the completion of the reaction was from 85 to 100 percent with various nitrites. In the present case the pressure change at completion varied considerably with the experimental conditions, as is shown by some typical pressure-time curves in Fig. 2. As a result it was no longer feasible to assume that a definite fixed pressure increase corresponded to complete reaction. All runs were therefore carried to completion, and the rate in any run was calculated from the time required for the pressure to increase 25 or 50 percent of the pressure increase at completion *in that particular run*.

The values of the pressure increase at completion are given in Table III together with the reaction rate data. It will be seen that at the higher pressures the percent pressure increase at completion is more or less independent of the temperature. At the higher temperatures, however, there is a very pronounced falling off in

TABLE I. *Typical experiments at 212.2°C.*

INITIAL PRESSURE = 24.7 cm				INITIAL PRESSURE = 6.55 cm			
Time (min.)	ΔP (cm)	% reaction	$K \times 10^3$ (sec.$^{-1}$)	Time (min)	ΔP (cm)	% reaction	$K \times 10^3$ (sec.$^{-1}$)
1	4.0	24.6	4.69	1	1.0	28.5	4.79
2	6.8	38.2	3.99	2	1.5	43	4.69
3	9.5	53.3	4.23	3	1.9	54	4.30
4	11.4	64.0	4.25	4	2.2	63	4.10
5	12.8	72.0	4.24	5	2.5	71.5	4.23
6	13.8	77.6	4.15	6	2.75	78.5	4.25
7	14.8	83.2	4.25	7	2.9	83	4.21
8	15.4	86.5	4.17	8	3.0	86	4.10
10	16.3	91.2	3.86	9	3.15	90	4.25
12	16.5	92.6	3.61	12	3.2	91	3.41
14	17.1	96.1	3.85	15	3.3	94	4.22

TABLE II. *Typical experiments at 191.5°C.*

INITIAL PRESSURE = 24.6 cm				INITIAL PRESSURE = 5.8 cm			
Time (min.)	ΔP (cm)	% reaction	$K \times 10^4$ (sec.$^{-1}$)	Time (min.)	ΔP (cm)	% reaction	$K \times 10^4$ (sec.$^{-1}$)
2	1.7	8.1	7.01	2	0.55	9.0	7.85
4	3.8	18.1	8.25	4	1.05	17.2	7.89
6	6.3	30.0	9.90	6	1.5	24.6	7.79
8	8.5	40.5	10.79	8	1.8	29.2	7.17
10	10.1	48.0	10.90	10	2.2	36.1	7.43
12	11.15	53.1	10.48	12	2.8	45.9	8.55
15	12.6	60.0	10.19	14	3.05	50.0	8.11
20	14.55	69.3	9.48	17	3.45	56.6	8.11
30	16.75	79.8	8.88	20	4.0	65.5	8.65
35	17.55	83.5	8.59	25	4.5	73.8	8.85
40	18.15	86.5	8.50				

pressure increase at lower pressures. The fact that carbon and tarry materials are formed suggests that the lower pressure increases are to be associated with some secondary condensation reaction.

THE RATE OF THE REACTION

Complete data for some typical experiments are given in Tables I and II. It is apparent from the tables that both at high and low pressures at 212.2° the constancy of K is quite satisfactory. At the lower temperature the constancy is still quite good at the lower pressures. At high pressures, however, K rises steadily to a maximum at about 50 percent reaction, and then falls again. This change in the form of the pressure-time curve with changing temperature may be expected to introduce some uncertainty into the calculated value of the temperature coefficient.

The summarized data for all runs are given in Table III. Runs marked P were made in a packed bulb. At the two lower temperatures it was not feasible to carry the runs to completion. It has therefore been assumed that the pressure increase at completion at these temperatures is equal to the mean value at 191.5°.

From the constancy of T_{25} and T_{50} at higher pressures it may be concluded that the reaction is definitely first order. The values of T_{25} and T_{50} vary considerably at lower pressures, however. In view of the change in the pressure increase at completion at lower pressures, it seems probable that the mechanism of the reaction is changing, and hence no great weight should be attached to the low pressure values. At higher pressures, however, the results are satisfactorily reproducible.

The runs marked P in Table III were made in a reaction vessel packed with short lengths of $\frac{1}{4}$ inch tubing. The surface/volume ratio for the packed vessel was about 6 times greater than for the empty vessel. It is apparent that no appreciable effect is produced by the increased surface. The reaction is thus homogeneous and unimolecular, and is therefore suitable for comparison with the other nitrite decompositions, although on account of its complexities we cannot expect very great accuracy in the calculated values of the velocity constant.

THE TEMPERATURE COEFFICIENT

From the foregoing discussion it is evident that only the results at the higher pressures are very trustworthy. Hence in calculating the temperature coefficient, we have used the mean values of T_{25} and T_{50} for all runs at pressures of 20 cm and over at each temperature. In Fig. 3 the logarithms of the fractional times are plotted against $1/T$. From the slopes of the lines we get 33,500 and 33,000 calories per gram mole respectively for the activation energy of the reaction.

It is apparent from the data of Tables I and II, and from similar data for all runs, that the initial rate of reaction, K_0, is equal to or slightly greater than K_{25} at high pressures and high temperatures, while at lower temperatures K_0 is considerably less than K_{25}. The result is that the temperature coefficient calculated from initial rates is somewhat higher than that calculated from T_{25} or T_{50}. It is difficult to make the extrapolation to initial rates with any certainty, but the results indicate that the true value of E

is in the neighborhood of 36,000 calories per gram mol, and hence agrees with the values previously found for the other nitrites.

On account of the uncertainty in the energy of activation, we cannot make a very direct

TABLE III. *The rate of reaction.*

P_0 (cm)	Final % ΔP	T_{25} (sec.)	T_{50} (sec.)	P_0 (cm)	Final % ΔP	T_{25} (sec.)	T_{50} (sec.)
Temperature = 212.2°C							
32.8	80	72	166	15.3	65	70	161
31.8	82	73	171	10.9	62	71	190
24.6	72	63	166	10.3	56	55	164
23.3	72	70	160	6.5	54	54	156
23.2	77	70	177	5.4	57	47	143
23.0	75	66	171	3.7	49	45	114
19.9	61	70	180	3.7	53	45	145
19.2	66	72	139	40.2P	83	81	158
18.0	67	72	180	34.3P	79	64	138
16.3	63	70	185	26.0P	73	80	175
16.0	64	70	163				
Temperature = 201.8°C							
33.3	73	171	317	13.6	77	183	414
32.0	82	153	296	13.4	73	176	396
29.0	76	158	315	13.3	69	195	405
27.8	78	120	310	9.3	57	183	500
25.7	75	166	330	9.2	65	155	395
25.6	83	168	340	8.8	58	201	428
25.0	80	167	316	8.5	67	177	465
24.7	72	137	330	8.4	62	220	525
22.3	73	185	354	7.2	65	188	520
21.5	79	168	323	6.7	65	158	403
19.6	73	166	363	38.3P	86	140	287
19.6	75	172	300	28.5P	80	176	339
18.2	78	177	402	20.7P	78	183	390
17.5	76	191	398	8.0P	67	248	464
15.8	66	216	450				
Temperature = 191.5°C							
43.2	82	253	740	18.8	76	347	690
33.7	77	260	600	17.8	78	347	675
29.8	82	274	669	14.8	78	347	675
28.6	79	300	640	8.3	75	458	960
25.6	85	300	660	5.5	65	444	1080
24.6	85	305	636	32.6P	80	330	660
23.7	79	303	600	25.2P	—	300	720
20.9	82	330	642				
Temperature = 181.3°C							
37.3	—	534	1770	5.8	—	1040	2115
29.2	—	612	1800	42.2P	—	640	1680
24.8	—	612	1775	35.5P	—	580	1500
22.1	—	640	1660	23.8P	—	640	1620
Temperature = 170.5°C							
35.3	—	1860	5640	22.1	—	1860	5460
25.2	—	1908	—	28.5P	—	1882	4980
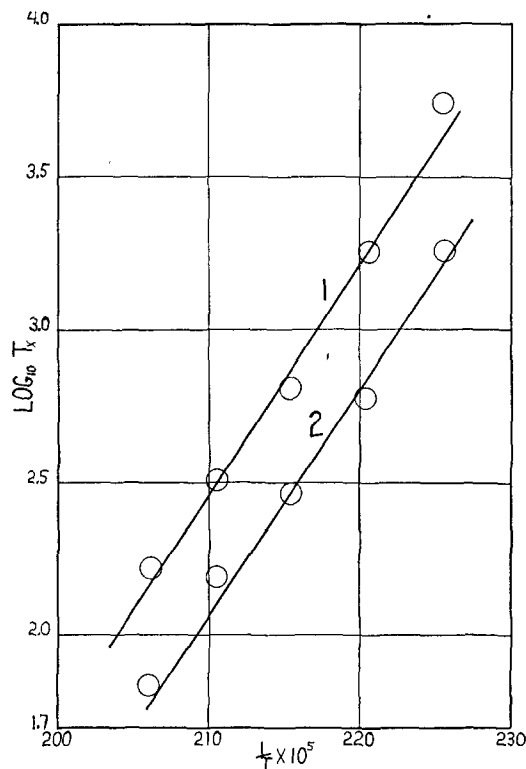
FIG. 3. Temperature coefficient.
1—T_{50}; 2—T_{25}.

comparison of its magnitude with that of the other members of the series, nor can we compare the values of the non-exponential factors in the expression for the rate. The safest method of procedure, therefore, is to compare the velocity constants at some arbitrarily chosen temperature. At 189.9°C, for example, we have

Substance	K, sec.$^{-1}$
Methyl nitrite	0.97×10^{-4}
Ethyl nitrite	1.89×10^{-4}
n-propyl nitrite	3.95×10^{-4}
iso-propyl nitrite	3.70×10^{-4}
n-butyl nitrite	8.88×10^{-4}

The marked regularity as we go up the series furnishes ample proof that the decomposition of butyl nitrite is strictly comparable to those of the others, and that the results have been correctly interpreted. The effect of the length of the hydrocarbon chain on the rate of reaction will be discussed in detail in a forthcoming communication.