

The Decomposition of Methyl Nitrite at High Pressures

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part be terminated by mechanism (B) rather than by (A). The result will be to raise the order of the reaction above 1, and thus give a rate which increases steadily with increasing pressure. In the present investigation the over-all order, as inferred from the effect of pressure on the rate, is about 1.35 and the results are therefore explicable on the basis of the free radical mechanism.

Unfortunately the situation is far too complicated to permit a quantitative comparison with the theory.

In conclusion we wish to express our indebtedness to the National Research Council of Canada for a studentship awarded to one of us (S. R.) during the tenure of which this work was performed.

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The Decomposition of Methyl Nitrite at High Pressures

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PREVIOUS work on the decomposition of diethyl ether at high pressures¹ showed that the rate increased continually with pressure up to 260 atmos., the rate at that pressure being about 40 times the previously calculated "high pressure rate." It has since been shown by Leermakers² that the reaction proceeds by a chain mechanism, as had been predicted by Rice and Herzfeld.³

The alkyl nitrites have been shown to decompose unimolecularly⁴ and it appears to be very unlikely that chains occur in these reactions.⁵ Nevertheless, it seemed worth while investigating the decomposition of methyl nitrite at high pressures to see if the rate would remain constant.

The apparatus, experimental procedure, preparation of materials, etc., were as previously described, except for the substitution of an oil bath for the lead bath owing to the lower temperatures required. The rates were inferred from the change in pressure accompanying the reaction. The results are given in Table I.

TABLE I. Temperature 217.5°C.

RUN No.	P_0 (cm)	k (sec. ⁻¹)	% ΔP AT COMPLETION
Steacie & Shaw	up to 65	1.0×10^{-3}	82.5
1	103	1.3	142
5	109	1.9	94
4	682	1.7	56
2	1320	1.7	118
3	2980	2.3	76
6 (Packed)	79	2.3	92

It is apparent that the pressure increase at completion is very erratic. The rate in run 6, where the surface is about double that in the empty vessel, is considerably higher than that in the corresponding unpacked runs, and the reaction is thus partly heterogeneous. Considerable error is also to be expected from gas law aberrations. In consequence the results are probably accurate only to within a factor of about 2. Furthermore most of the errors will tend to make the rate high. Hence it may be concluded that, within the rather large experimental error, there is no appreciable increase in the rate of decomposition of methyl nitrite on going from 65 cm to 35 atmos. This furnishes further support to the conclusion that the reaction is really unimolecular.

We wish to acknowledge our indebtedness to the National Research Council of Canada for a studentship awarded to one of us (S. R.) during the tenure of which this work was performed.

¹ Steacie and Solomon, *J. Chem. Phys.* **2**, 503 (1934); Steacie, Hatcher, and Rosenberg, *ibid.*, this issue.

² Leermakers, *J. Am. Chem. Soc.* **56**, 1899 (1934).

³ F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.* **56**, 284 (1934).

⁴ Steacie and Shaw, *Proc. Roy. Soc.* **A146**, 388 (1934); **A151**, 685 (1935); *J. Chem. Phys.* **2**, 345 (1934); **3**, 344 (1935).

⁵ F. O. Rice and Radowskas, *J. Am. Chem. Soc.* **57**, 350 (1935).