446. *Thermal Decomposition of* trans-*Dimeric Nitrosoalkanes.**

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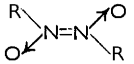
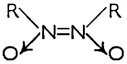
The gas-phase reaction *trans*-$(R{\cdot}NO)_2 \longrightarrow 2R{\cdot}NO$ has been studied for the cases $R = Me$ and Bu^i. A flow system has been employed and a spectrophotometric method developed for determining the amount of decomposition. The frequency factors and activation energies are discussed.

It has been demonstrated that primary [1,2,3] and secondary [3] nitrosoalkanes are capable of more than transitory existence and can form two different dimers which exhibit geometrical isomerism about the N=N bond. The *trans*-dimer (I) is more volatile than the *cis*-dimer (II), and both absorb in the ultraviolet in the region 260—300 mμ: the absorption maxima are separated by about 11 mμ (aqueous solution) and both compounds have a high intensity of absorption ($\varepsilon_{max.}$ ~10,000). These data have been summarised by Gowenlock and Lüttke.[4] When a stream of nitrogen containing monomeric nitrosoalkanes passes through a trap cooled in liquid oxygen the nitrosoalkane is condensed (presumably as the monomer): when this condensed material is allowed to warm to room temperature, a transition occurs [2,3,5] in the region of —78° and the *cis*-dimer results. These observations suggested that the rate of decomposition of the *trans*-dimer could be studied in the following manner; if a stream of nitrogen in which a *trans*-dimer is entrained is passed through a heated reaction vessel then some decomposition to the monomer will occur. Both compounds can be removed from the gas stream by condensation in liquid oxygen. Warming to room temperature will result in the transformation of the monomer into *cis*-dimer, and, after removal of the nitrogen, the two dimers may be separated by vacuum-sublimation and estimated by absorption spectrophotometry, aqueous solutions being used in order to prevent any reaction *cis* ⟶ *trans* which occurs in organic solvents.[2,3] The experimental method to be described applies these aspects of the chemistry of nitroso-compounds to the determination of the rate of reaction.

(I)





(II)

Experimental

trans-Dimeric nitrosomethane and *trans*-dimeric 2-methyl-1-nitrosopropane were prepared from pyrolysis products of t-butyl and isopropyl nitrite (nitrosomethane) and the nitrite derived from 4-methylpentan-2-ol (2-methyl-1-nitrosopropane) according to the method of Gowenlock and Trotman.[2,3] The products were purified by sublimation in nitrogen to constant vapour pressure. By this technique crystals about 6 mm. long can be built up if a source of gentle heat is present at one side of the trap. The nitrogen employed in the runs was either " white spot " nitrogen or prepared from thermal decomposition of sodium azide. The perfluorocyclohexane was a gift from Professor J. C. Tatlow and had been purified by vapour-phase chromatography.

Apparatus.—The apparatus used was that described by Chilton and Gowenlock.[6] For the runs where perfluorocyclohexane was added into the nitrogen flow, the apparatus was slightly modified to include manometers at the exit and the entrance of the reaction vessel and a capillary-leak for controlling the flow of the additive which entered the flow system between the Warhurst saturator traps [7] containing the dimer and the reaction vessel.

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* A preliminary account of some of this work was published in the *Chem. Soc. Special Publ.*, No. 10, 1957, p. 75.

[1] Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516.

[2] Gowenlock and Trotman, *J.*, 1955, 4190.

[3] Gowenlock and Trotman, *J.*, 1956, 1670.

[4] Gowenlock and Lüttke, *Quart. Rev.*, 1958, **12**, 321.

[5] Chilton and Gowenlock, *J.*, 1953, 3232; 1954, 3174.

[6] Chilton and Gowenlock, *Trans. Faraday Soc.*, 1953, **49**, 1451.

[7] Warhurst, *Trans. Faraday Soc.*, 1939, **35**, 674.

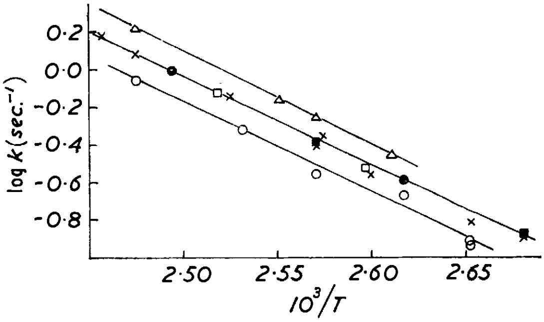
Calibration Run.—With the reaction vessel at room temperature, the product in the collecting traps could be vacuum-sublimed in its entirety, and the aqueous solution gave the ultraviolet absorption spectrum of the pure *trans*-dimer. The optical density at the absorption maximum was measured by using either a Unicam S.P. 500 or a Hilger Uvispek Spectrophotometer, 1 cm. cells being used in either case. Aqueous solutions of the dimer were made up to either 500 or 1000 ml. by distilled water.

Pyrolysis Runs.—(a) *Nitrogen carrier gas.* The technique used for estimation of % decomposition was based upon that described in the introduction: for the isobutyl compound the separation of the two dimers by vacuum-sublimation was more difficult than for nitrosomethane, since the *cis*-compound had a slight volatility.

(b) *Nitrogen carrier gas with approximately* 0·5 *mm. of perfluorocyclohexane.* On completion of the run, the nitrogen carrier gas was pumped from the system, and then the liquid-oxygen baths around the product traps were removed. The *trans*-dimer and perfluorocyclohexane were removed by vacuum-sublimation. A further separation of the C_6F_{12} from the *trans*-dimer was then attempted by vacuum-sublimation from −60°, at which temperature the C_6F_{12} could be slowly sublimed to a liquid-oxygen trap. However, complete separation by this method was not possible as some *trans*-dimer was always entrained with the C_6F_{12}. The two dimers were dissolved in known volumes of distilled water, and their concentrations determined spectrophotometrically.

FIG. 1. *Plot of* log *k against* 1/*T for nitrosomethane.*

△ *Total pressure* ~8 *mm.*
● *Total pressure* ~4 *mm.*; *packed reaction vessel.*
○ *Total pressure* ~4·5 *mm.* (~4 *mm. nitrogen*, ~0·5 *mm.* C_6F_{12}).
× *Total pressure* ~4 *mm.*; *reaction time* ~1 *sec.*
□ *Total pressure* ~4 *mm.*; *reaction time* ~2·9 *sec.*
■ *Total pressure* ~4 *mm.*; *partial pressure decreased by a factor of* 7.



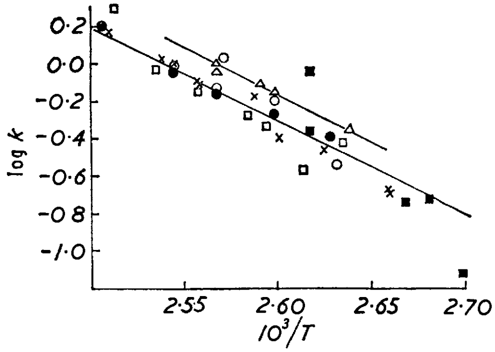


FIG. 2. *Plot of* log *k against* 1/*T for nitrosoisobutane.*

△ *Total pressure* ~8 *mm.*
× *Total pressure* ~4 *mm.*; *reaction time* ~1 *sec.*
■ *Total pressure* ~4 *mm.*; *reaction time* ~2·9 *sec.*
○ *Total pressure* ~4 *mm.*; *partial pressure increased by a factor of* 2.
□ *Total pressure* ~4 *mm.*; *partial pressure decreased by a factor of* 3.
● *Total pressure* ~4 *mm.*; *packed reaction vessel.*

Calculation of Results.—The percentage decomposition was obtained from the molar fraction *cis*-dimer/(*cis*-dimer + *trans*-dimer). The numerator was obtained from the spectrophotometric determination of the *cis*-dimer; the denominator was obtained from the vapour-pressure calibration. The sum of the experimentally determined values for the denominator is in excellent agreement with that obtained from the calibration runs except in the case of the addition of C_6F_{12} where two vacuum-sublimations were required (see above). The reaction time was calculated from the flow rates of the carrier gas, temperature, pressure, and reaction-vessel volume. All results are expressed as first-order velocity constants.

Results.—These are shown in Figs. 1 and 2.

DISCUSSION

In a nitrogen flow system without addition of the fluorocyclohexane the first-order velocity constants are the same (apart from random scatter) within the following limits: (*a*) Nitrosomethane partial pressure of dimer 4×10^{-3}—10^{-2} mm.; reaction time 0·9—3 sec.; alteration of surface : volume ratio by a factor of 12. (*b*) 2-Methyl-1-nitrosopropane partial pressure 3×10^{-4} to 2×10^{-3} mm.; reaction time 0·9—3 sec.; alteration of surface : volume ratio by a factor of 12. For both substances an increase in nitrogen pressure from 4·2 to 8 mm. gives an increase of about 35% in the velocity constant. We are of the opinion that the reaction is of the first order and that therefore there is no contribution from a reverse reaction under our conditions. The variation in rate constant with total pressure is ascribed to the fact that the reaction is in the region where there are insufficient collisions to maintain an equilibrium concentration of activated molecules. In this connection our use of the fluoro-additive was made to see if the activation energy and Arrhenius factor would be markedly different in the presence of an inert molecule with many degrees of freedom: such a molecule would be expected to maintain the reaction at a position of true unimolecularity. The efficiency of nitrogen as an energy-transfer agent is known to be low. However, reference to Fig. 1 shows that addition of perfluorocyclohexane has little, if any, effect on the reaction rate or the kinetic parameters. This is in marked contrast to the effect of the additive on the rate of decomposition of monomeric nitrosomethane.[8] The data listed in Table 3 show the variations of the activation energy and Arrhenius factor (as determined by least mean squares plots).

TABLE 3. *Activation energies and Arrhenius factors for* $(R{\cdot}NO)_2 \longrightarrow 2R{\cdot}NO$.

R	Pressure	*E* (kcal. mole^{-1})	$\log_{10} A$ (sec.$^{-1}$)	R	Pressure	*E* (kcal. mole^{-1})	$\log_{10} A$ (sec.$^{-1}$)
Me	4·2	21·7	11·8	Bu^i	4	25·6	14·2
	8	23·0	13·4		8	25·6	14·4
	4 mm. (N_2) + 0·5 mm. (C_6F_{12})	22·0	11·8				

The error limits in the activation energies are estimated to be ±1·5 kcal. mole^{-1} on the basis that the largest inherent error in the method is that due to estimation of the percentage decomposition. The corresponding error limit in $\log_{10} A$ (sec.$^{-1}$) is ±0·8. We can therefore claim that the activation energies for the decomposition reaction are 22·2 ± 2 kcal. mole^{-1} (methyl) and 25·6 ± 1·5 kcal. mole^{-1} (isobutyl).

The pressure range that we have employed is of the order to be expected for the region of the commencement of the well-known Lindemann fall-off characteristics, and we suggest that the measurements are in the region of the limiting high-pressure rate and that activation energies can therefore be related to the difference in structure between the monomer and the dimer. Following the basis provided by Keussler and Lüttke [9] and adopted by us elsewhere,[10] we ascribe the relatively low activation energy for breaking the N=N double bond to the energy compensation provided by electron rearrangements at the nitrogen atoms when two molecules of monomer are formed from one molecule of the *trans*-dimer. The activation energy for the reverse reaction will be small, the value of 6 kcal. mole^{-1} given by Calvert, Thomas, and Hanst [11] being of the order suggested by us elsewhere.[10] Although there are two values [11,12] given for the rate constant for the reverse reaction ($k_{25} = 87$ l. mole^{-1} sec.$^{-1}$; $k_{16\text{-}20} = 12$ l. mole^{-1} sec.$^{-1}$), the two techniques employed are quite different and no reasonable value of the activation energy can be obtained from them.

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[8] Batt, Thesis, Birmingham, 1959.

[9] Keussler and Lüttke, *Z. Elektrochem.*, 1959, **63**, 614.

[10] Batt and Gowenlock, *J.*, 1960, 376.

[11] Calvert, Thomas, and Hanst, *J. Amer. Chem. Soc.*, 1960, **82**, 1.

[12] Christie, *Proc. Roy. Soc.*, 1958, *A*, **249**, 258.

It is not yet possible to make an unambiguous correlation for the differences between the stabilities of different nitroso-compounds. Certainly the differences in activation energy for decomposition seem quite small [9,10,13,14] but it is our opinion that solvent effects are important and that generalisation must await a thorough investigation of the decomposition in a variety of solvents. We may note that Arrhenius factors determined in this work indicate that little, if any, of the rigidity of the *trans*-dimeric nitroso-group [cf. (I)] is lost on formation of the transition state.

Extension of this technique to other *trans*-dimeric nitrosoalkanes is limited to primary and secondary alkyl groups (t-alkyl dimers do not have a *cis*-configuration). Some dimers are too involatile (*e.g.*, nitrosocyclohexane), whereas others are liquids at room temperature (*e.g.*, nitrosoethane) and tend to form the isomeric oxime when kept. It therefore seems probable that only a limited extension is possible, *e.g.*, to the *trans*-dimers of 2-nitrosopropane and 1-nitrosobutane.

One of us (J. T.) thanks the Department of Scientific and Industrial Research for a Maintenance Grant, and another (L. B.) thanks the University of Birmingham for an Appeals Fund Scholarship.

The University, Birmingham, 15.

[*Received, November 5th,* 1959.]

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[13] Anderson and Hammick, *J.*, 1935, 30.
[14] Schwartz, *J. Amer. Chem. Soc.*, 1957, **79**, 4353.