

562. *Decomposition Rates of Some Tertiary trans-Dimeric C-Nitroso-compounds.*

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The rates of disappearance of some tertiary *trans*-dimeric C-nitroso-compounds have been measured spectrophotometrically in a variety of solvents and solvent mixtures. The relation between the heat of activation and the entropy of activation is discussed. Reasons for the greater stability of dimeric 3-methyl-3-nitrosopentan-2-one in the presence of water are discussed. Quantitative comparison of the stabilities of different nitroso-compounds is best made by the extrapolation of the activation heat-entropy graphs, to give the heat of activation at zero entropy of activation.

It is known¹ that there are wide variations in the rate of the reaction $\text{trans}-(\text{R}\cdot\text{NO})_2 \longrightarrow 2\text{R}\cdot\text{NO}$ when R is altered, also¹⁻³ that, for any *trans*-dimeric nitroso-compound, alteration in the solvent results in different heats and entropies of activation. Thus, any correlation of structure with decomposition rate and/or Arrhenius parameters must be such as to comprehend this solvent effect. Recent work has shown⁴ that spectrophotometric

¹ Batt and Gowenlock, *Trans. Faraday Soc.*, 1960, **56**, 1022.

² Schwartz, *J. Amer. Chem. Soc.*, 1957, **79**, 4353.

³ Batt and Gowenlock, *J.*, 1960, 376.

⁴ Gowenlock and Redish, *Z. phys. Chem. (Frankfurt)*, 1962, **31**, 169.

measurements of the removal rates of primary and secondary *trans*-dimeric nitroso-compounds are liable to misinterpretation because of the influence of both the reverse reaction and the isomerization of the monomeric nitroso-compound to the oxime upon the time-dependence of the dimer concentration. Such misinterpretation may be avoided by the use of tertiary dimers: the isomerization then does not occur and the use of low dimer concentrations obviates the kinetic complications due to the onset of equilibrium.³ Thus we are able to correlate the effect of change of R on decomposition rate, using the same solvent in every case, and to investigate the linear $\Delta H^\ddagger - \Delta S^\ddagger$ variation^{2,3} for change of solvent with constant R. Also the reduction of the decomposition rate of some *trans*-dimeric nitrosocompounds on addition of water^{1,2} required explanation.

The suitability of a tertiary nitroso-compound is, in part, determined by the temperature-range of the available thermostat-controlled spectrophotometer. Schwartz² was able to measure the decomposition rate at 5° for the dimers where R = CMe₂Et and Me₂C·CH₂·O·COMe, but when R = Bu^t and Me₂C·NO₂ the reaction was too fast for measurement. It was decided to study again the dimers with R = Me₂C·COMe and Me₂C·CH₂·COMe,⁵ where a CH₂ group is interposed in front of the carbonyl group with marked effect on the dissociation rate;⁶ also we studied the effect of varying R to MeEtC·COMe.

EXPERIMENTAL AND RESULTS

Kinetic measurements were made as previously,³ the variation of optical density at the wavelength of maximum absorption with time being measured. The temperature range was 21—67°. The first-order rate constants were independent of initial optical density. The log (optical density)—time plots were accurately linear; the products gave no absorption under our conditions; and, in general, decompositions of up to 80% could be employed.

Dimeric 3-methyl-3-nitrosobutan-2-one was prepared by Batt and Gowenlock³ and used without further purification. Dimeric 3-methyl-3-nitrosopentan-2-one was made by the method of Aston, Menard, and Mayberry.⁷ Dimeric 4-methyl-4-nitrosopentan-2-one was made by oxidation of diacetoneamine with monoperoxysulphuric acid.⁸ The spectroscopic solvents (cyclohexane, anhydrous ethanol, acetonitrile, carbon tetrachloride, chloroform, dioxan, water) were either obtained commercially or purified by standard methods. Ethanol-water and dioxan-water mixtures were prepared by mixing known volumes; in some cases a check on the proportion of water in the mixture was obtained from a refractive-index measurement and comparison with the published composition-refractive index values.

The temperature-dependence of the velocity constants is shown in Figs. 1—3, and Table 1 lists the Arrhenius parameters, and the heat of activation (ΔH^\ddagger) and the entropy of activation (ΔS^\ddagger) derived from substitution in the equation⁹

$$k_1 = (kT/h) \exp -\Delta H^\ddagger/RT \exp \Delta S^\ddagger/R, \text{ where } \Delta H^\ddagger = E_{\text{Arrhenius}} - RT.$$

The values of Anderson and Hammick⁵ and of Batt and Gowenlock³ are included in this Table.

The Table shows wide variations in ΔH^\ddagger and ΔS^\ddagger with solvent for the two dimers. For dimeric 4-methyl-4-nitrosopentan-2-one in anhydrous solvents the heat of activation and the entropy are related linearly, as for the two tertiary dimers investigated by Schwartz^{2,3} (see Fig. 4). However, for reactions in ethanol-water and dioxan-water and in water, the points lie in an apparently random manner above the $\Delta H^\ddagger - \Delta S^\ddagger$ isokinetic line.¹⁰ The addition of water implies therefore either a smaller entropy or a greater heat of activation, relative to non-aqueous solvents, or a combination of the two effects. If we consider the effect as being due solely to a decrease in ΔS^\ddagger at a constant ΔH^\ddagger , and represent this decrease by $\Delta(\Delta S^\ddagger)$, then

⁵ Anderson and Hammick, *J.*, 1935, 30.

⁶ Sidgwick (revised by Taylor and Baker), "Organic Chemistry of Nitrogen," Oxford Univ. Press, 1937, p. 207.

⁷ Aston, Menard, and Mayberry, *J. Amer. Chem. Soc.*, 1932, **54**, 1530; 1935, **57**, 1888.

⁸ Bamberger, *Ber.*, 1900, **33**, 1781.

⁹ Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 199.

¹⁰ Leffler, *J. Org. Chem.*, 1955, **20**, 1202.

smooth relations between $\Delta(\Delta S^\ddagger)$ and the proportion of water in both solvent mixtures are revealed (see Fig. 5). This is also true if the comparable increase in ΔH^\ddagger at a constant ΔS^\ddagger

TABLE 1.
Arrhenius parameters for the reaction $(R\cdot NO)_2 \rightarrow 2R\cdot NO$.

R	Solvent	Activation energy (kcal. mole ⁻¹)	Log ₁₀ Arrhenius factor (sec. ⁻¹)	ΔH^\ddagger (kcal. mole ⁻¹)	ΔS^\ddagger (e.u.)
Me ₂ C·CH ₂ ·COMe	Ethanol	29.9	18.63	29.3	24.4
"	Acetonitrile	22.0	13.00	21.4	-1.3
"	Chloroform	29.7	18.37	29.1	23.2
"	Dioxan	26.3	16.20	25.7	13.5
"	Carbon tetrachloride	25.5	15.70	24.9	11.3
"	Benzene ⁵	24.0	14.56	23.4	7.9
"	Water	28.0	15.40	27.3	9.7
"	Ethanol-water 22:78	27.6	15.53	27.0	10.1
"	" 66.5:33.5	25.3	14.48	24.7	6.7
"	" 44.5:55.5	26.2	15.05	25.6	8.0
"	" 78:22	28.1	16.95	27.5	16.7
"	Dioxan-water 25:75	30.0	16.78	29.3	18.2
"	" 50:50	29.2	17.25	28.6	18.3
"	" 75:25	26.3	15.75	25.7	11.5
Me ₂ C·COMe	Ethanol ³	28.0	15.51	27.4	10.4
"	Cyclohexane ³	28.3	16.11	27.7	13.2
"	Carbon tetrachloride ³	30.2	17.27	29.6	18.6
"	Chloroform	31.0	17.73	30.4	20.1
"	Dioxan	32.7	18.75	32.1	25.1
"	Acetonitrile	28.4	14.81	27.8	7.0
MeEtC·COMe	Chloroform	28.9	16.32	28.2	13.7

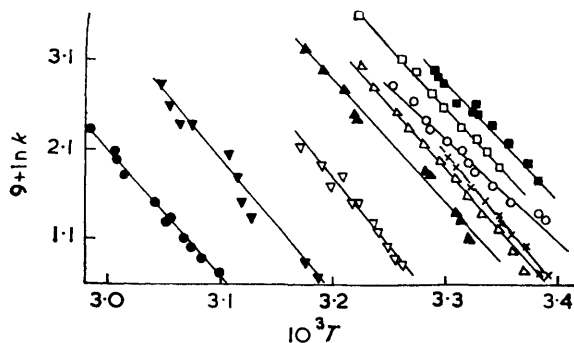


FIG. 1. Temperature-dependence of velocity constants for $(R\cdot NO)_2 \rightarrow 2R\cdot NO$ ($R = Me_2C\cdot CH_2\cdot COMe$.) (a) In pure solvents: \times EtOH, \circ MeCN, Δ $CHCl_3$, \bullet H_2O , \square dioxan, \blacksquare CCl_4 ; (b) in dioxan-water: \blacktriangledown 25:75, ∇ 50:50, \blacktriangle 75:25.

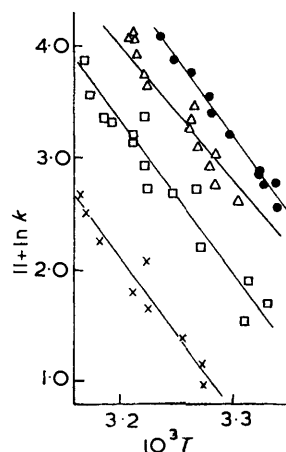


FIG. 2. Temperature-dependence of velocity constants for $(R\cdot NO)_2 \rightarrow 2R\cdot NO$ ($R = Me_2C\cdot CH_2\cdot COMe$) in ethanol-water: \times 22:78, \square 44.5:55.5, Δ 66.5:33.5, \bullet 78:22.

[i.e., $\Delta(\Delta H^\ddagger)$] is plotted against the proportion of water (see Fig. 6). The heat of activation-entropy values for dimeric 3-methyl-3-nitrosobutan-2-one are presented in Fig. 4; with the exception of acetonitrile, the relation between these values is again linear.

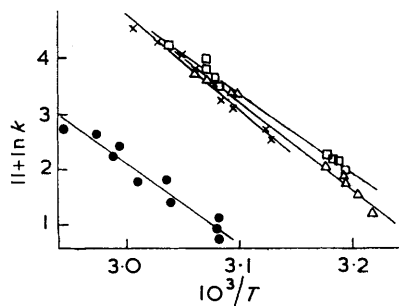


FIG. 3. Temperature-dependence of velocity constants for $(R\cdot NO)_2 \rightarrow 2R\cdot NO$. (a) $R = Me_2C\cdot COMe$: \times dioxan, \bullet MeCN, Δ $CHCl_3$; (b) $R = MeEtC\cdot COMe$, \square $CHCl_3$.

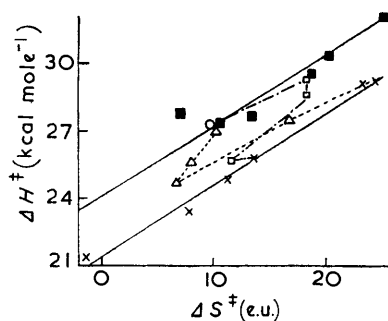


FIG. 4. $\Delta H^\ddagger/\Delta S^\ddagger$ relation for $(R\cdot NO)_2 \rightarrow 2R\cdot NO$. (a) $R = Me_2C\cdot CH_2\cdot COMe$: \times non-aqueous solvents; o H_2O ; Δ EtOH- H_2O ; \square Dioxan- H_2O ; (b) $R = Me_2C\cdot COMe$: \blacksquare non-aqueous solvents.

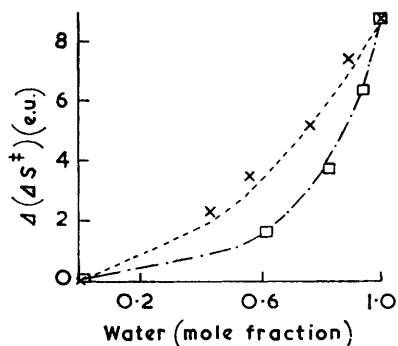


FIG. 5. Plot of $\Delta(\Delta S^\ddagger)$ against mole fraction of H_2O for $(R\cdot NO)_2 \rightarrow 2R\cdot NO$ ($R = Me_2C\cdot CH_2\cdot COMe$). \times EtOH- H_2O ; \square Dioxan- H_2O .

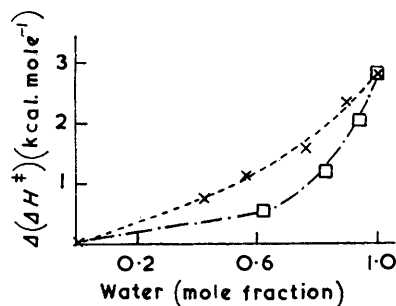


FIG. 6. Plot of $\Delta(\Delta H^\ddagger)$ against mole fraction of H_2O for $(R\cdot NO)_2 \rightarrow 2R\cdot NO$ ($R = Me_2C\cdot CH_2\cdot COMe$). \times EtOH- H_2O ; \square Dioxan- H_2O .

DISCUSSION

The significance of the results and our interpretation of them depends on the size of the experimental errors. In general these are small (± 0.1 – 0.2 kcal. mole $^{-1}$) in relation to the differences (7 kcal. mole $^{-1}$) in activation energies for the same compound in different solvents. The Arrhenius plots show a greater scatter for the solvent mixtures and we refer to this below.

Linear ΔH^\ddagger - ΔS^\ddagger Relations.—Four dimeric tertiary aliphatic C-nitroso-compounds exhibit this linear interdependence of heat of activation and entropy. This cannot be ascribed to failure of experimental technique, as for each compound a single, standardized procedure with the same apparatus and same observer has been followed. We therefore consider that the variations are genuine and require explanation in terms of a model of the reaction. This may be provided by the energy diagram (Fig. 7) based upon previous discussions.^{3,11,12} Curve I represents the energy curve for the decomposition of the dimer where the valency state of the nitrogen atoms is maintained as in the dimer. Repulsion between two dipolar molecules of monomer is represented by curve II and the crossing-point of the two curves gives the transition state. It is reasonable to assume that the

¹¹ Gowenlock, Trotman, and Batt, *Chem. Soc. Special Publ.* No. 10, 1957, p. 75.

¹² Keussler and Lüttke, *Z. Elektrochem.*, 1959, **63**, 614.

repulsion between two molecules of monomer will be modified by the solvent. Curve III represents such a modification which implies a greater activation energy for the decomposition. This will result in a larger N-N separation in the transition state and it is reasonable to associate this with increased rotational freedom about the stretched N-N bond. A higher entropy of activation will then result. It is known¹² that for five different dimers there is a considerable entropy gain (36—41 e.u.) on passing from the dimer to two monomer molecules. The entropies of activation which we have obtained

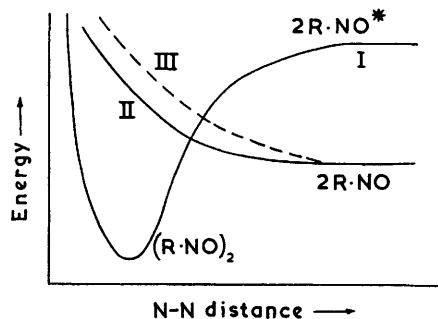


FIG. 7. Potential-energy diagram for dissociation of $(R\cdot NO)_2$. I, Dissociation to give two molecules of "excited" monomer, N atoms in same valency state as in dimer; II, repulsion between two molecules of monomer; III, modification of curve II on alteration of solvent.

are less than this quantity (-1 to $+25$ e.u.) and thus our explanation is reasonable and in agreement with known data. Of course, this picture may be oversimplified but it affords a simple rationalization of the linear $\Delta H^\ddagger - \Delta S^\ddagger$ plot in that an increase in ΔH^\ddagger is proportional to an increase in ΔS^\ddagger . It carries a further implication, that deviations from the $\Delta H^\ddagger/\Delta S^\ddagger$ isokinetic line are related to an extra stabilizing or destabilizing factor: to this we shall return in discussing the water effect.

The isokinetic line can be applied to the comparison of the stabilities of different dimers. In an earlier survey,¹¹ we implied that comparison of Arrhenius parameters in a common solvent would supply such data. Table 2 shows that this is not possible because both ΔH^\ddagger and ΔS^\ddagger vary.

TABLE 2.

Activation heat and entropy data for $(R\cdot NO)_2 \longrightarrow 2R\cdot NO$ in chloroform solution.

R	Me ₂ CEt	Me ₂ C-CH ₂ -O-COMe	Me ₂ C-COMe	Me ₂ C-CH ₂ -COMe	MeEtC-COMe
ΔH^\ddagger (kcal. mole ⁻¹)...	27.7	23.6	30.4	29.1	28.2
ΔS^\ddagger (e.u.)	17.9	7.8	20.1	23.2	13.2

A common practice for comparison of reactivities is the comparison of velocity constants at a fixed temperature. However, if both the activation parameters vary it is possible for the relative velocity constants to lie in different sequences depending on the temperature that is chosen. We therefore suggest that a more useful comparison is afforded by the isokinetic lines for the different dimers whereby the activation heats at a chosen standard entropy of activation can be measured. This eliminates the solvent effects which may be arranged in a different order for the different dimers. If we make our comparison at a zero entropy of activation, that is, at the same torsional rigidity as in the dimer initial state, we obtain the values for ΔH^\ddagger given in Table 3.

TABLE 3.

ΔH^\ddagger at $\Delta S^\ddagger = 0$ for $(R\cdot NO)_2 \longrightarrow 2R\cdot NO$.

R	Me ₂ CEt	Me ₂ C-CH ₂ -O-COMe	Me ₂ C-CH ₂ -COMe	Me ₂ C-COMe
ΔH^\ddagger (kcal. mole ⁻¹)	21.8	21.2	21.4	23.5

Because of associated errors the first three examples may be regarded as virtually coincident, and the "great stability" ⁶ of demeric 3-methyl-3-nitrosobutan-2-one compared

with that of dimeric 4-methyl-4-nitrosopentan-2-one is an energy difference of only 2 kcal. mole⁻¹. The attributed "great stability" was based on qualitative observation of blue colours (monomer) and on cryoscopy in benzene. It thus appears that relatively small energy differences can produce considerable qualitative and quantitative differences. The results agree with the fact that blue colours, although not visible to the naked eye,⁶ may nevertheless be detectable by a sensitive spectrophotometer.¹² Our earlier contention¹¹ that comparison of dimer stabilities should be on a quantitative basis is thus upheld.

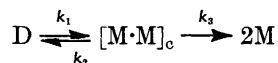
If we assume that decomposition of dimeric primary and secondary nitroso-compounds affords the isokinetic relationship, the $\Delta H^\ddagger - \Delta S^\ddagger$ line having slopes of the same order as those reported here, then our earlier results¹ give the following values for ΔH^\ddagger at $\Delta S^\ddagger = 0$: when R = Bu^t, sec-C₅H₁₁, cyclohexyl, Ph·CH₂, Ph·CH₂·CH₂, $\Delta H^\ddagger = 25 \pm 1$ kcal. mole⁻¹; when R = Me, $\Delta H^\ddagger = 27 \pm 1$ kcal. mole⁻¹. Rowe's values¹³ for nitrosomesitylene imply that $\Delta H^\ddagger = 19 \pm 1$ kcal. mole⁻¹. Table 4 shows the parallelism between these activation heats and the heats of equilibrium measured by Keussler and Lüttke.¹²

TABLE 4.
Comparison of heats of activation (forward reaction) and equilibrium (ΔH)
for $(R \cdot NO)_2 \rightleftharpoons 2R \cdot NO$.

R	2,4,6-C ₆ H ₂ Me ₃	Me ₂ C·COMe	Ph·CH ₂	Cyclohexyl
ΔH (kcal. mole ⁻¹)	12.1	18.9	20.4	20.6
ΔH^\ddagger (at $\Delta S^\ddagger = 0$) (kcal. mole ⁻¹) ...	19 ± 1	23.5	27 ± 1	27 ± 1

The Water Effect.—We suggested above that deviation from the isokinetic line is due to an extra stabilizing or destabilizing effect. Fig. 4 shows that water decreases the rate of decomposition. The variation in the activation parameters (see Table 1 and Fig. 4) is seemingly random, though ΔH^\ddagger and ΔS^\ddagger pass through minimum values for ethanol-water solutions. Figs. 5 and 6 show, respectively, that $\Delta(\Delta S^\ddagger)$ and $\Delta(\Delta H^\ddagger)$ show a smooth increase with the proportion of water present in the solvent. Such increases can be related to greater torsional rigidity of the transition state in the presence of water, to solvation of the dimer by water with only a relatively small solvation of the transition state, or to both effects. However, it is not apparent why this effect should depend upon the proportion of water present, because, as the dimer is present in concentrations of $>10^{-4}$ mole l.⁻¹, solvation should be complete with only small quantities of water. Admittedly, Figs. 5 and 6 involve two separate errors, as $\Delta(\Delta S^\ddagger)$ and $\Delta(\Delta H^\ddagger)$ represent differences between different experimental values, but the general trend of the results is significant and real, though the degree of curvature of the plots may be only approximate. We suggest that the deviations represented in Figs. 5 and 6 represent a function of the total solvent composition rather than a function of the solvation of the molecule.

Water has a greater degree of structure than the other solvents employed in our kinetic studies and it seems possible that the addition of water to either ethanol or dioxan corresponds to the formation of structural units in the solvent which then form a "cage" surrounding the dimer molecule. Goates and Sullivan¹⁴ have suggested that the thermodynamic properties of dioxan-water mixtures can be explained by the existence of different hydrogen-bonded "structons" of varying composition. Such cages of solvent molecules would be formed around the dimer molecule and the two monomer units and for complete reaction it would be necessary for the two monomer units to diffuse out of the cage. On such a basis the kinetic scheme is similar to that given by Benson:¹⁵



¹³ Rowe, *Diss. Abs.*, 1959, **20**, 1143.

¹⁴ Goates and Sullivan, *J. Phys. Chem.*, 1958, **62**, 188.

¹⁵ Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, 1960, p. 544.

where $[M \cdot M]_c$ represents two molecules of monomer present as near neighbours in the same solvent cage. For a stationary concentration of $[M \cdot M]_c$ we have

$$-d(D)/dt = k_1(D) \cdot k_3 / (k_2 + k_3)$$

The $\Delta(\Delta S^\ddagger)$ and/or $\Delta(\Delta H^\ddagger)$ terms are to be associated with the extra entropy and heat terms involved in this mechanism, in particular, with the diffusion-controlled removal of two monomer molecules from their solvent cage. The feasibility of such cages operating in the decomposition is clarified by molecular models. It can be shown that dimeric 4-methyl-4-nitrosopentan-2-one can be so disposed in space that the hydrogen atoms of a single water molecule can come into close contact with the carbonyl-oxygen atom of one half of the molecule and the bisnitroso-oxygen atom of the other half of the molecule, and thus the feasibility of some stabilizing hydrogen-bonded cage structure is supported. The greater scatter of the Arrhenius plots for the solvent mixtures can reasonably be associated with the variation of structure in the solvent with alteration of temperature.

A summary of some of the conclusions in this paper has appeared elsewhere.¹⁶ J. K. thanks the University of Birmingham for a post-graduate scholarship.

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¹⁶ Gowenlock and Kay, *Z. Elektrochem.*, 1961, **65**, 713.