72. *Kinetic and Structural Studies of* trans-*Dimeric* 3-*Methyl*-3-*nitrosobutan*-2-*one.*

By L. Batt and B. G. Gowenlock.

The rates of disappearance of *trans*-dimeric 3-methyl-3-nitrosobutan-2-one in ethanol, cyclohexane, and carbon tetrachloride solution have been measured spectrophotometrically. The reaction is irreversible under the conditions of low dimer concentration. The results are discussed in relation to Keussler and Lüttke's equilibrium studies and Jensen and Berg's dipole-moment measurements.

Dimeric 3-methyl-3-nitrosobutan-2-one was first obtained by Aston, Menard, and Mayberry [1] from the products ensuing when gaseous ethyl nitrite was passed through isopropyl methyl ketone containing hydrochloric acid. These authors stated that monomer production in organic solvents was slow, and this was later compared [2] with Anderson and Hammick's [3] determination of the rate of monomer production from dimeric 4-methyl-4-nitrosopentan-2-one in benzene. It was asserted that this was due to the different substituent effects in $(Me_2CX{\cdot}NO)_2$ where X = Ac or CH_2Ac, which were

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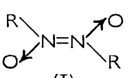
[1] Aston, Menard, and Mayberry, *J. Amer. Chem. Soc.*, 1932, **54**, 1530.

[2] Sidgwick (revised by Taylor and Baker), " Organic Chemistry of Nitrogen," Oxford, 1937, p. 207.

[3] Anderson and Hammick, *J.*, 1935, 30.

believed to modify the electronic effect of the acetyl group by the interposition of the CH_2 group. In a previous publication,[4] we accepted this qualitative statement and tabulated the available evidence (Table 3 of ref. 4). In this and succeeding papers we shall relate such statements to energy and entropy measurements of the depolymerisation.

Jensen and Berg's [5] dipole-moment measurements of dimeric 3-methyl-3-nitrosobutan-2-one in dioxan and benzene gave μ 3·38 and 3·32 D respectively (at 25°), which are much larger than expected for the *trans*-dimeric configuration (I), for, when $R = Me$, $\mu \leqslant 0{\cdot}6$ D,[6] and when $R = Bu^i$, $\mu \leqslant 0{\cdot}7$ D [7] (a *cis*-structure is unlikely since tertiary alkyl *cis*-dimers are unknown [8]). However, although Lüttke [9] has shown that for carbon tetrachloride solutions the characteristic frequency for the monomeric $-N{=}O$ group appears in the infra-red region, for benzene solutions (initial dimer concentrations of 10^{-1} mole l.$^{-1}$) the equilibrium constant for the dissociation is only $6{\cdot}86 \times 10^{-6}$ mole l.$^{-1}$ at 20°—this was obtained from observations of the intensity of the n–π^* (N) transitions.[10] This very small equilibrium constant suggested that monomer formation could not be invoked to explain Jensen and Berg's value for the dipole moment.



(I)

EXPERIMENTAL

Kinetic measurements were made by observing the variation of the optical density with time for the dimeric nitroso-compound. A Unicam SP.500 spectrophotometer was used in conjunction with an Adkins cell-holder in a thermostat.[11] Stoppered silica cells (1 cm.) containing the solvent (cyclohexane, ethanol, or carbon tetrachloride) were inserted into the block, whose temperature had been measured by means of a copper–constantan thermocouple. After ~20 min., it having been observed that the cells were optically paired, one cell was removed, a little of the nitroso-compound added, the whole shaken vigorously for about 20 sec. to ensure complete dissolution, and the cell re-inserted in the block. Readings of the optical density were then taken at regular intervals and from the plot of the logarithm of the optical density against time (which was accurately linear) the first-order velocity constant was obtained (the products gave no absorption under our experimental conditions). After each run the temperature was again measured. The optical densities fell within the range 1—0·2; the wavelengths employed were 295 mμ (ethanol), 297 mμ (cyclohexane), 299 mμ (carbon tetrachloride). The temperatures fell within the range 32—49·5°. The rate constants were independent of initial optical density and, as the molar extinction coefficient is of the order 10^4, the concentrations of dimer employed were of the order 2—10×10^{-5} mole l.$^{-1}$. The rate constants were independent of percentage decomposition; percentage decompositions of 15—50% were employed.

Dimeric 3-methyl-3-nitrosobutan-2-one was made according to the method of Aston, Menard, and Mayberry [1] and was recrystallised by precipitating it from chloroform solution by dropwise addition of light petroleum (b. p. 60—80°). The spectroscopic solvents were obtained commercially.

Dipole-moment measurements were made in an apparatus based upon that described by Bender,[12] and the results were calculated by Guggenheim's method.[13] Benzene was purified by storage over fresh sodium wire, followed by repeated crystallisation.

RESULTS AND DISCUSSION

The results are given in Table 1, and Table 2 gives the parameters obtained from the best straight line and from the conversion to the Glasstone, Laidler, and Eyring [14] parameters ΔH^* and ΔS^*.

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[4] Gowenlock, Trotman, and Batt, Chem. Soc. Special Publ. No. 10, 1957, p. 75.
[5] Jensen and Berg, *Annalen*, 1941, **548**, 110.
[6] Smith, *J.*, 1957, 1124.
[7] *Idem*, personal communication.
[8] Gowenlock and Trotman, *J.*, 1956, 1670.
[9] Lüttke, *Z. Elektrochem.*, 1957, **61**, 302.
[10] Keussler and Lüttke, *Angew. Chem.*, 1958, **70**, 442; *Z. Elektrochem.*, 1959, **63**, 614.
[11] Eaborn, *J.*, 1956, 4858.
[12] Bender, *J. Chem. Educ.*, 1946, **23**, 179.
[13] Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714; 1951, **47**, 573.
[14] Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 199.

We shall first discuss these results in relation to the dissociation process and Keussler and Lüttke's equilibrium data. Fig. 1 is a potential-energy diagram for the dissociation process and is based upon Lüttke's original suggestion.[15] Comparison with Keussler and Lüttke's equilibrium data (ΔE = 18·9 kcal. mole^{-1}, ΔS = 43 e.u.) indicates that the back-reaction has an activation energy of about 8—10 kcal. mole^{-1} and thus the crossing point of the potential curves (I) and (II) in Fig. 1 is such as to indicate only small repulsion between the two monomer units in forming the transition state. Explanation for the absence of the back-reaction under our conditions must therefore be sought elsewhere. The importance of the entropy of activation must be stressed. The " high " frequency (Arrhenius) factor for the forward reaction indicates that the transition state is looser than the initial state. It is known that the dimeric N_2O_2 structure is rigid and therefore we can associate this entropy increase with the onset of some freedom of partial rotation about the stretched N=N bond in the transition state. However, for the back-reaction there will be considerable decrease in entropy on formation of the transition state (25—33 e.u.). This will result in a steric factor of the order of 10^{-7}. Under our experimental conditions, the small concentration of dimer, the small percentage decomposition, and the dependence of the rate of the back-reaction on the square of the monomer concentration are the major reasons for the unimportance of the back-reaction: these combine to produce very slow equilibration.

TABLE 1. *Velocity constants.*

In ethanol solution		In cyclohexane		In carbon tetrachloride	
Temp.	10^3k (min.$^{-1}$)	Temp.	10^3k (min.$^{-1}$)	Temp.	10^3k (min.$^{-1}$)
32°	1·50	32·0°	3·71	32·0°	2·61
36·6	2·98	33·3	4·86	34·0	3·69
36·6	3·02	36·6	7·47	36·1	4·95
38·5	4·31	38·8	11·8	38·7	7·14
38·5	5·18	40·8	14·4	40·1	9·85
41·5	7·54	44·0	24·9	42·9	14·3
43·9	9·32	45·9	32·2	45·9	22·0
45·9	15·0	46·6 *	28·3	45·9	22·2
46·6 *	12·9	47·9	39·8	48·4	34·9
47·9	16·1	48·8	43·2		
49·5	17·5				

* Preliminary result only.

TABLE 2. *Kinetic results.*

[$k_{1st\ order} = (kT/h) \exp -\Delta H^*/RT \exp \Delta S^*/R$, where $\Delta H^* = E_{Arrhenius} - RT$]

Solvent	Activation energy (kcal. mole^{-1})	Arrhenius factor (sec.$^{-1}$)	ΔH * (kcal. mole^{-1})	ΔS * (e.u.)
Ethanol	28·0 ± 0·5	3·27 × 10^{15}	27·4	10·4
Cyclohexane	28·3 ± 0·5	1·29 × 10^{16}	27·7	13·2
Carbon tetrachloride	30·2 ± 0·2	1·86 × 10^{17}	29·6	18·6

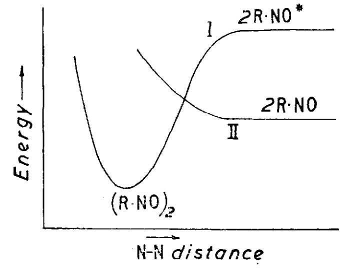

FIG. 1. *Potential energy diagram for dissociation of* (R·NO)$_2$.

The difference between the three solvents may be attributed to solvation and dipolar

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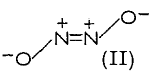
[15] Lüttke, Habilitationsschrift, Freiburg i. Br., 1956.

attraction. It is possible that carbon tetrachloride solvates the transition state to a smaller extent than the other two solvents and that this accounts for the larger activation energy. Ethanol and cyclohexane have almost identical activation energies, but the smaller entropy of activation for the ethanol case suggests a dipolar attraction in the transition state between ethanol and the stretched framework (II) which increases the rigidity of this framework relative to cyclohexane solution.


(II)

The only kinetic data for tertiary nitroso-compounds have been given by Anderson and Hammick[3] and by Schwartz.[16] The former investigated the rates of dissociation of 4-methyl-4-nitrosopentan-2-one in benzene, the temperature range being almost 14°. The energy of activation (24 kcal. mole^{-1}) is significantly lower than for our carbonyl compound, as is also the entropy of activation. Schwartz measured the energy and entropy of activation from the rates of dissociation of 2-methyl-2-nitrosobutane and of 1-acetoxy-2-methyl-2-nitrosopropane in six solvents over a temperature range of either 7° or 12°. Unfortunately, there are several errors in the original paper. Table 3 presents the recalculated values[17] for ΔH^* and ΔS^*, and shows that there is a relatively small solvent effect for the second case. We conclude that our original assertion[4] that the aliphatic dimers which dissociate " readily " at room temperature have activation energies in the 21—25 kcal. mole^{-1} range is supported by these data. Fig. 2 shows a plot of ΔH^* values against ΔS^*. These lie on a straight line, and the point derived from Hammick and Anderson's kinetic data lies on it. Our own values, which also exhibit a linear relationship, are displaced from the continuous line drawn in Fig. 2. Discussion of the significance of these free-energy relations is deferred until results are available for a wider range of nitroso-compounds.

TABLE 3. $(MeCX{\cdot}NO)_2 \longrightarrow 2Me_2CX{\cdot}NO$.

	$X = Me{\cdot}CO_2$		$X = Et$	
Solvent	ΔH^* (kcal. mole^{-1})	ΔS^* (e.u.)	ΔH^* (kcal. mole^{-1})	ΔS^* (e.u.)
$Ph{\cdot}NO_2$	27·5	21·9	20·9	−3·3
MeOH	20·4	−2·8	22·6	1·7
Me_2CO	23·9	9·8	23·6	6·7
$Me{\cdot}CO_2Et$	24·3	11·5	23·1	5·3
$CHCl_3$	23·6	7·8	27·7	17·9
C_6H_6	25·8	16·0	24·3	9·4

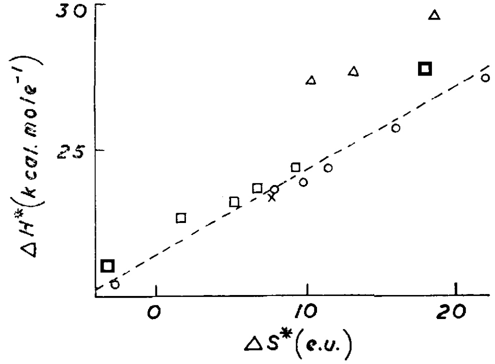


FIG. 2. *Plot of* ΔH^* *against* ΔS^*.
○ *Schwartz's values for* $(Me{\cdot}CO_2{\cdot}CMe{\cdot}NO)_2$.
□ *Schwartz's values for* $(Me_2CEt{\cdot}NO)_2$.
× *Hammick's value for* $(Me{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}NO)_2$.
△ *Our values for* $(Me{\cdot}CO{\cdot}CMe_2{\cdot}NO)_2$.

It remains to discuss Jensen and Berg's dipole-moment measurements.[5] Our initial expectation was that their values would prove to be in error and that the " true " value would be in accord with data obtained from other *trans*-dimers.[6,7] Our values are compared with Jensen and Berg's in Table 4: good agreement is obtained.

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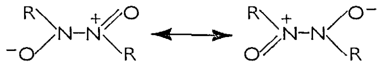
[16] Schwartz, *J. Amer. Chem. Soc.*, 1957, **79**, 4353.
[17] *Idem*, personal communication.

TABLE 4. *Polarisation measurements for* trans-(R·NO)$_2$ *in benzene.*

R	P_{A+O} (c.c.)	Temp.	Ref.	R	P_{A+O} (c.c.)	Temp.	Ref.
Me	7·5	25°	6	Me_2C·COMe ...	236·6 (222 [a])	25	5
Bu^i	10·15	25	7	Me_2C·COMe ...	223	20	This paper

[a] Recalcd. by Guggenheim's method.

No weight can be given to Jensen and Berg's suggestion that their dipole moment values support the resonance formulæ (III), whose inadequacy has been treated elsewhere.[18] The large polarisation cannot be due to atom polarisation alone (an upper limit of about 50 c.c.

(III) 

can be set on this). The polarisation must therefore be due to free rotation about the C–C and C–N bonds, resulting in a very wide range of possible conformations ranging from those in which the C=O dipoles are in complete opposition to those in which they lie almost parallel. Calculation of the dipole moment according to Smythe and Walls's method [19] gives [7] μ 3·97 D, a value higher than that obtained from our results (μ 3·29 D). This discrepancy is usual for molecules with interference to free rotation,[20] and construction of molecular models indicates some restricted rotation due to the close approach between the carbonyl and the nitrosyl oxygen atoms.

Jensen and Berg state that decomposition of the dimer is catalysed by light. However, our kinetic measurements revealed no difference in the rates of removal of dimer when (*a*) the standard technique (illumination only during the time of the reading—never greater than 5% of the time) and (*b*) continuous illumination of the cell was used.

We are indebted to Dr. J. W. Smith for permission to quote unpublished results and for a helpful discussion of dipole-moment data, to Dr. Schwartz for permission to quote corrected results, and to Dr. Lüttke for many discussions of the mechanism of dimer decomposition. One of us (L. B.) acknowledges the award of an Appeals Fund Scholarship.

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[18] Gowenlock and Lüttke, *Quart. Rev.*, 1958, **12**, 321.
[19] Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 2261.
[20] Smith, " Electric Dipole Moments," Butterworths, London, 1955, p. 293.