Tetrahedron Vol. 34, pp. 2591–2596
© Pergamon Press Ltd., 1978. Printed in Great Britain

0040–4020/78/0815–2591/$02.00/0

KINETICS OF THE DISSOCIATION AND *CIS–TRANS* ISOMERIZATION OF *o,o'*-AZODIOXYTOLUENE (DIMERIC *o*-NITROSOTOLUENE)

MICHEL AZOULAY and GUNNAR WETTERMARK
Division of Physical Chemistry, The Royal Institute of Technology,
S-100 44 Stockholm 70, Sweden

(*Received in UK* 13 *March* 1978; *Accepted for publication* 30 *March* 1978)

Abstract—The dimer-monomer reactions were investigated for the system *cis* and *trans o,o'*-azodioxytoluene-*o*-nitrosotoluene in acetonitrile solvent. For the reaction *cis* dimer-monomer the following thermodynamic and activation parameters have been derived: $\Delta H^\circ = 58.5 \pm 2.5$ kJ mole^{-1}, $\Delta S^\circ = 206.2 \pm 3.8$ J mole^{-1} K^{-1}, $\Delta H^{\neq} = 63.6 \pm 3.3$ kJ mole^{-1}, $\Delta S^{\neq} = 6.3 \pm 0.3$ J mole^{-1} K^{-1}. The corresponding values for the reaction *trans* dimer-monomer are: $\Delta H^\circ = 45.6 \pm 2.1$ kJ mole^{-1}, $\Delta S^\circ = 162.7 \pm 7.1$ J mole^{-1} K^{-1}, $\Delta H^{\neq} = 80.8 \pm 2.9$ kJ mole^{-1}, $\Delta S^{\neq} = -13.4 \pm 0.8$ J mole^{-1} K^{-1}. There is no evidence of a direct *cis–trans* isomerization (i.e. a reaction not proceeding via the monomer). NMR and various perturbation techniques monitoring the visible absorption of the monomer were employed.

C-Nitroso compounds readily associate to dimeric form—azodioxy compounds.[1-3] In the solid state some compounds crystallize as monomers, others as dimers.[4-9] Mixed crystals with both monomer and dimer are also known. The nitroso species are strongly coloured, whereas the dimers show no absorption in the visible.[10] The monomer-dimer equilibrium may be strongly affected by the temperature,[11-14] thus these nitroso-azodioxy systems exhibit the phenomenon of thermochromism. The thermodynamics for this equilibration in solution has been studied by Lüttke, using visible absorption spectrophotometry.[14]

The dimer may undergo *cis–trans* isomerization[14-17] and a reaction scheme of the type shown in Fig. 1 then applies. Hitherto the *cis–trans* isomerization has not been observed to proceed directly, but only via the monomer. However, so far the studies have included aliphatic compounds, in particular nitrosocyclohexane and nitrosomethane.[16,17] Aromatic compounds may possibly have a conjugation between the N=N bond and the aromatic ring which could lower the barrier to rotation about the N=N bond. The present work embraces a detailed mechanistic and kinetic study of the dissociation reaction and the *cis–trans* isomerization of an aromatic derivative, namely, *o,o'*-azodioxytoluene. The *trans* and *cis* isomers of this material can be isolated in the crystalline form.[18] The present studies involved the use of rapid dilution and equilibration methods as well as NMR band-shape analysis.

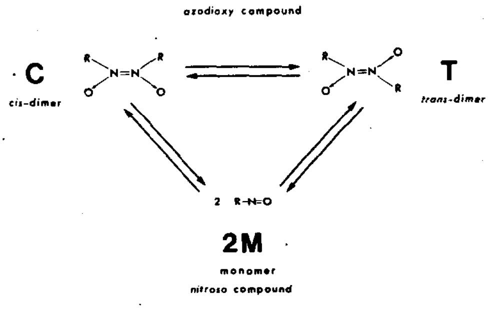


Fig. 1. Reaction scheme for the dissociation and *cis–trans* isomerization of azodioxy compounds.

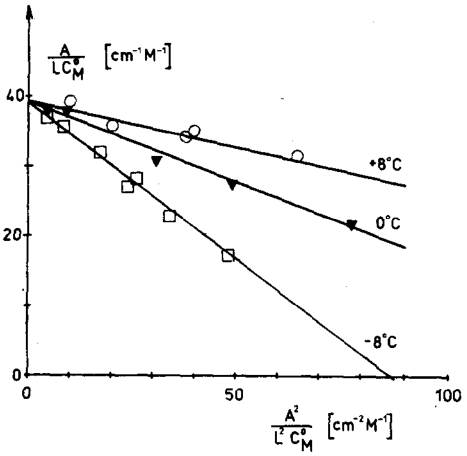


Fig. 2. Spectrophotometric measurements of the overall equilibrium dimer⇄monomer of *o,o'*-azodioxytoluene in acetonitrile at three temperatures.

RESULTS

Equilibrium studies using spectrophotometry

The dimer–monomer equilibrium was investigated spectrophotometrically using the specific visible absorption band of the monomer. The global equilibrium constant K for the overall dissociation reaction:

$$D \rightleftarrows 2M \tag{1}$$

is related to the global degree of dissociation α as

$$K = \frac{2\alpha^2}{1-\alpha} C_M{}^0 \tag{2}$$

$\alpha = \bar{C}_M/C_M{}^0$ $(0 \le \alpha \le 1)$ is the ratio of the monomer concentration of equilibrium to the total concentration expressed in monomer units $C_M{}^0 = C_M + 2C_D$ with C_M and C_D monomer and dimer concentration.

Using eqn (2) together with Lambert Beer's law, a linear function should be obtained between $A(LC_M{}^0)^{-1}$

and $A^2(L^2C_M^0)^{-1}$ according to:

$$\frac{A}{LC_M^0} = -\frac{2}{K\epsilon}\cdot\frac{A^2}{L^2C_M^0}+\epsilon \qquad (3)$$

where A = absorbance, L = path length, ϵ = absorption coefficient of the monomer.

Results obtained at three temperatures are shown in Fig. 2. From the intercept and the slope, values of K and ϵ are found as given in Table 1.

Dynamics of equilibration

Dissolving crystals of pure *trans* dimer and measuring the light absorption of the monomer revealed a time dependence as shown in Fig. 3(a). The concentrations chosen were so low so as to make the contribution from the association process negligible. Similar experiments with crystals of pure *cis* dimer yielded monomer, this reaction being too fast to record.

Conduction of concentration-jump relaxation experiments using the stopped-flow technique showed a two-step relaxation process, i.e. a fast and a slow reaction (see Fig. 3b). Both steps were exponential, the first (I) being about two orders of magnitude faster than the slower (II). The second step has rates identical to those found in the experiments dissolving pure *trans* crystals.

Table 1. Equilibrium constant values for the overall dissociation reaction (1) determined from NMR and spectrophotometry

Temperature [°C]	K (NMR) [M]	K (SPECTROPH.) [M]
− 8.0	0.13 ± 0.03	0.128 ± 0.007
0.0	0.26 ± 0.06	0.236 ± 0.009
+ 8.0	0.50 ± 0.12	0.465 ± 0.011

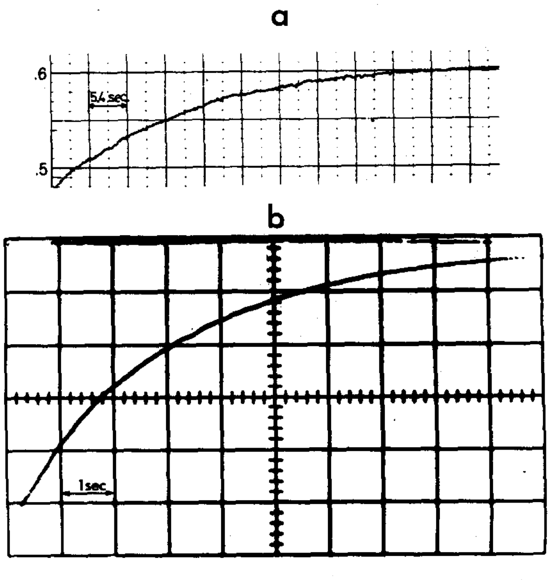
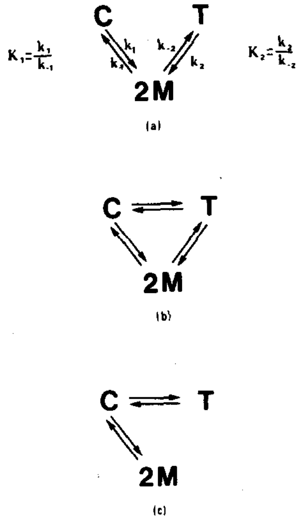


Fig. 3. (a) The absorbance (λ = 775 nm) of a solution prepared by dissolving *trans* crystals of *o,o'*-azodioxytoluene in acetonitrile at 10°C measured vs time. (b) The time dependence of the transmittance (λ = 660 nm) of an acetonitrile solution of *o,o'*-azodioxytoluene subjected to a concentration-jump from 0.5 to 0.25 M (C_M^0). A two step relaxation was observed and only the fast step (I) is displayed in the figure.

The results suggest reaction paths of the type shown in Scheme 1.



Scheme 1. Possible reaction paths for the *cis–trans* isomerization.

The relaxation of the cis *species from stopped-flow measurements*

For dimerization reactions it is possible to perform a concentration-jump experiment by suddenly increasing or decreasing the total concentration of the solution at constant temperature. The stopped-flow technique, whereby a solution of concentration $2C_M^0$ was diluted to C_M^0, was used to evaluate the fast-reaction step, i.e. the relaxation of the *cis* species. The same technique did not prove to be fruitful for evaluating the kinetics of the slow step (relaxation of the *trans* dimer) owing to stability problems with the single-beam detection system over longer periods of time.

The stopped-flow technique represents a large perturbation of the total concentration. However, in the present system the relative change in monomer concentration during each step is small enough to permit the use of the relaxation equation

$$\tau_I^{-1} = k_I + 4k_{-I}\bar{C}_M. \qquad (4)$$

Owing to experimental limitations, only a small concentration range could be covered. A clear concentration dependence was not exhibited over this range, 0.25 M ≤ $C_M^0(\infty) \leq 0.50$ M. This is not surprising, since the $4k_{-I}\bar{C}_M$ term in eqn (5) is considerably smaller than k_I, as evidenced by the equilibrium measurements (Fig. 7). Furthermore, as the experimental accuracy in the determination of τ is about ±10%, any slight concentration dependence existing in τ would not show up. Plots of $\ln\ln[(V_\infty/V_t)]$ against time were linear (within 99% confidence) according to the equation $\ln\ln(V_\infty/V_t) = -t/\tau_I + \ln\ln[(V_\infty/V_0)]$, where V_∞ and V_t refer to signal-intensity values measured relatively to the dark voltage (0% transmission). The V_∞-signal was recorded immediately after the single-run recording. Only runs where the V_∞ was constant (to the eye) were taken into consideration. Experiments were carried out at four temperatures and the values of τ_I are entered in the Eyring plots (Fig. 4).

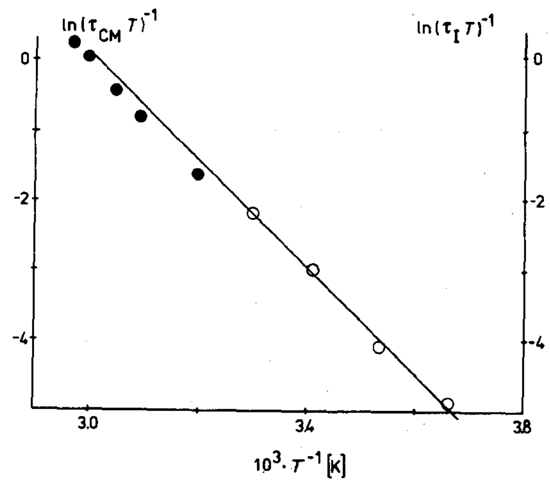


Fig. 4. Eyring plots for the reaction C→2M of *o,o'*-azodioxytoluene in acetonitrile measured by the stopped-flow technique (right scale, open circles) and by NMR (left scale, filled circles).

Decay of the trans *species*

Equilibration measurements. Equilibration measurements of the *trans* dimer were made, dissolving pure *trans* crystals and measuring the light absorption (see above) at five different temperatures, viz. 4.7, 9.8, 11.2, 15.5 and 20°. The absorbance of the monomeric species was monitored. Since the solutions were extremely diluted (≤ 0.02 M) the equilibrium position was shifted far towards monomer.

The dissociation rate constant for the *trans*-dimer→monomer reaction was evaluated from least square curve fittings of the exponential curves according to the equation:

$$A_t = A_\infty - (A_\infty - A_0)\exp(-k_{II}t) \qquad (5)$$

where A_t, A_∞, A_0 stands for absolute absorbances at time t, an infinity, and at the selected zero time. Obtained values of k_{II} are given in Fig. 5.

Relaxation of the trans *species from rapid dilution using an injection syringe.* From *ca* 1 M nitroso solutions thermostated at 20°, 50μl-aliquots were withdrawn with a rapid-dispensing syringe. Each aliquot was rapidly injected into a 1 cm cell placed in the thermostated holder of a double-beam spectrophotometer. The cell contained 2.50 ml of pure solvent, acetonitrile, and injection was given at a height of about 1 cm from the bottom of the cell. The solvent was kept at a constant temperature of 20°. The time elapsing between the injection and the recording of the relaxation process was less than 2 sec. Only one exponential step was obtained, yielding a rate constant value identical to that obtained when dissolving the *trans* powder at 20° (see Fig. 5).

NMR investigations

NMR spectra. The Me proton NMR spectrum of *o,o'*-azodioxytoluene was investigated over the temperature range 20–73°. It exhibited band-shape changes as shown in Fig. 6. The spectra shown relate to CD_3CN as solvent, but similar spectra were obtained in $CDCl_3$ and CH_2Cl_2. However, the lower b.ps of the latter solvents prevented their use at the higher temperatures. Three peaks were observed at room temperature. These are labelled T, C for *trans* and *cis* *o,o'*-azodioxytoluene and M for

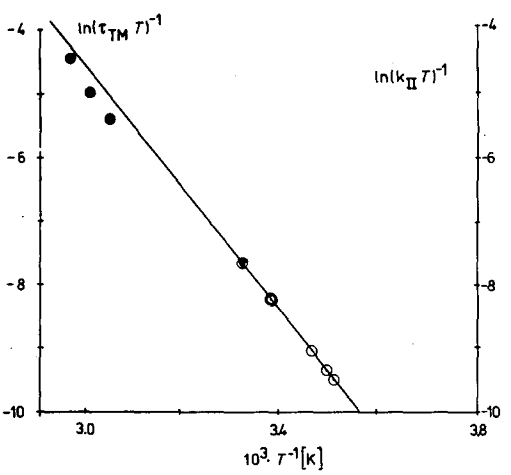


Fig. 5. Eyring plots for the reaction T→2M of *o,o'*-azodioxytoluene in acetonitrile using spectrophotometry (right scale, open circles) and NMR (left scale, filled circles). The spectrophotometry involved dissolving pure *trans* crystals and recording the function of monomer through its strong absorption in the visible. The results from one experiment using the technique of rapid dilution are also given (right scale, triangle).

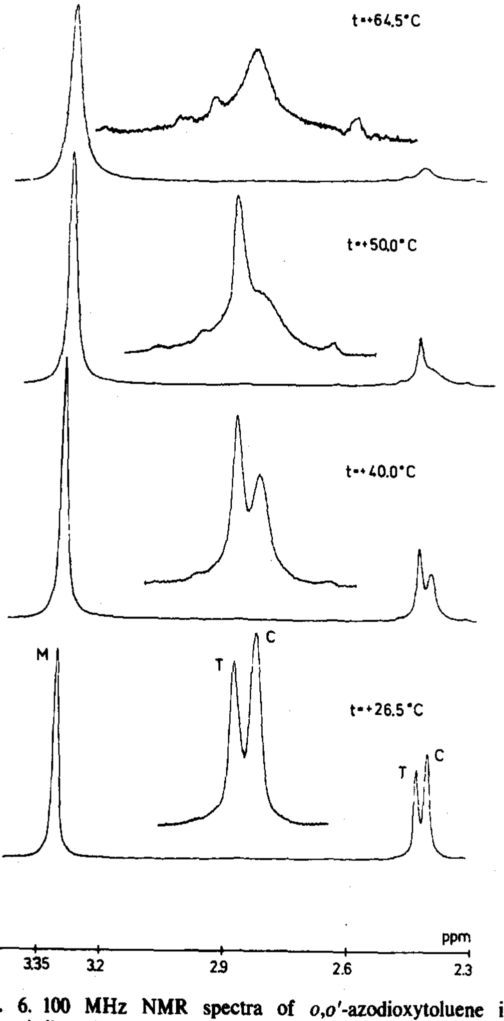


Fig. 6. 100 MHz NMR spectra of *o,o'*-azodioxytoluene in acetonitrile. The spectra around 2.4 ppm are shown expanded and enhanced as inserts.

monomer species (*o*-nitrosotoluene) (cf Fig. 1). Assignments were based on measurements of solutions prepared by dissolving pure *cis* or *trans* crystals, cf Ref. 18†.

On raising the temperature, the most marked broadening is seen for peak C. Thus at 40° the effect on C is clearly seen, but the temperature has to be raised to about 50° before T broadens. At this temperature the band shape of C has drastically changed. The monomer resonance is broadened only at the highest temperatures, cf spectrum at 64.5°C.

An apparent "coalescence" of the two dimer peaks occurs at these temperatures. The reported changes are reversible when lowering the temperature. However, a small irreversible process also takes place at the highest temperatures, cf the spectrum at 64.5°, presumably owing to thermal disproportionation of the azodioxy compound.

NMR spectra of dilute solutions (having the equilibrium position shifted well towards the monomer) prepared by dissolving *cis* or *trans* crystals at −60° (in $CDCl_3$) yielded only the peak of the respective dimer. The monomer peak gradually appears, but that of the other dimer never occurs in observable amounts. For mechanism 1c to apply, the *cis–trans* population ratio must be extremely small to be consistent with this observation. However, from the equilibrium measurements (see below) it is known to be greater than unity.

Model for the chemical exchange. The observed changes of the NMR spectra indicate that C exchanges directly with the monomer. This agrees well with the spectrophotometric equilibration measurements of the fast reaction between *cis* dimer and monomer (step I). The equilibrium *trans* dimer ⇄ monomer is attained more slowly, as is shown consistently by the various experimental findings. The results of the spectrophotometric relaxation measurements speaks in favour of two relaxation steps with about the same low activation entropy values. The activation enthalpy is lower than one would expect for a direct *cis–trans* process. The NMR data were thus analyzed assuming reaction Scheme 1a to apply.

Computation of kinetic and equilibrium data from NMR. Thermodynamic and kinetic parameters were evaluated by complete bandshape analysis of the NMR spectra. The theoretical band shapes were calculated using a computer program based on the McConnell equation for three exchange sites without coupling.[20] The rates of exchange for the association process are related by:

$$P_M \sum \frac{1}{\tau_{Mi}} = \sum P_i \frac{1}{\tau_{iM}} \qquad (6)$$

where P_M and P_i values, i = C, T, denoted the populations of protons on the sites M, C and T and

$$P_M + P_C + P_T = 1. \qquad (7)$$

Note that $P_M = \bar{C}_M/C_M{}^\circ = \alpha$ (overall degree of dissociation). The chemical exchange life time τ_{Mi} and τ_{iM} are related to the rate constants k_μ ($\mu = 1, 2$) by the equations

$$\begin{aligned} \tau_{Mi} &= C_M{}^{-1}k_{-\mu}^{-1} \\ \tau_{iM} &= k_\mu{}^{-1}. \end{aligned} \qquad (8)$$

The theoretically calculated band shapes were fitted to the experimental curves using a three-site model. However, only the exchanges T⇔M and C⇔M were considered in accordance with the selected model for the chemical exchange (the τ-values related to C⇔T exchange were kept constant at 10000 s). The values of the relaxation time T_2 were set equal for the *cis* and *trans* peaks as observed experimentally. The chemical shifts for the various sites are given in Table 2.

Evaluation of thermodynamic and activation parameters

The ΔH°_μ and ΔS°_μ values ($\mu = 1, 2$) associated with the reactions $C \rightleftarrows 2M$ and $T \rightleftarrows 2M$ were evaluated from the NMR data using linear plots of $\ln K_\mu$ vs T^{-1} and ΔG°_μ vs T, respectively (Fig. 7). These thermodynamic parameters are shown in Table 3.

As a test of the consistency of the results obtained from the various experimental techniques, K values evaluated from NMR are compared with those obtained from spectrophotometry.

In this comparison, values of K_1 and K_2 were estimated from extrapolation of the NMR data to the temperatures −8, 0 and +8° and used for calculating K according to the relation:

$$K = K_1K_2/(K_1 + K_2). \qquad (9)$$

The results are presented in Table 1 together with the K-values evaluated from the spectrophotometric method, cf Fig. 2.

The NMR chemical exchange lifetimes τ_{iM} were used to calculate the activation parameters ΔH^+, ΔS^+ and ΔG^+ from the Eyring equation (assuming a transmission coefficient of unity):

$$(\tau T)^{-1} = kh^{-1}\exp(-\Delta H^+(RT)^{-1})\exp(\Delta S^+R^{-1}). \qquad (10)$$

Plots of $\ln(\tau_{iM}T)^{-1}$ vs T^{-1} are shown in Figs. 4 and 5. The activation parameters are collected in Table 3.

Table 2. Chemical shifts (in ppm) relative to TMS as internal references for 2 M solutions of nitroso compound measured at 100 MHz, +26.5°C in CD_3CN

M	C	T
3.292	2.437	2.411

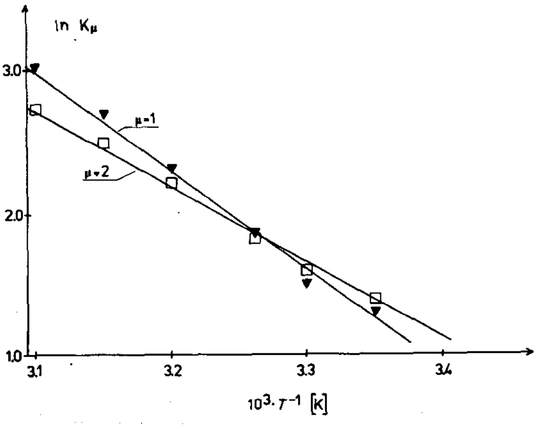


Fig. 7. Equilibrium constants for the reactions $C \rightleftarrows 2M$ and $T \rightleftarrows 2M$ of *o,o'*-azodioxytoluene in acetonitrile.

---

†It should be noted that the labelling of the peaks is different from that used in Ref. 19. Definite assignments of the peaks were not possible at the time of the studies reported in Ref. 19.

Table 3. Thermodynamic and kinetic parameters for the dissociation processes of *o,o'*-azodioxytoluene in acetonitrile. For comparison the corresponding values for azodioxycyclohexane obtained from Ref. 17 are included in parentheses. UV and VIS refer to spectrophotometry in the ultraviolet and visible, respectively.* Stopped-flow-concentration jump.** Equilibration starting with the pure *trans* isomer[a]

Process	Method for detection	$\Delta G^{o}_{300.2}$ b) kJ/mole^{-1}	ΔH^{o} kJ/mole^{-1}	ΔS^{o} J mole^{-1}K^{-1}
$C \rightleftarrows 2M$	NMR	-3.34	58.5±2.5	206.2±3.8
	(UV)	(26.3)	(72.8±5.9	(149±21)
$T \rightleftarrows 2M$	NMR	-3.26	45.6±2.1	162.7±7.1
	(VIS)	(36.4)	(82.4±16.7)	(154±21)
		$\Delta G^{\ddagger}_{300.2}$ c)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$C \rightarrow 2M$	NMR	61.5	66±7	14±20
	VIS*	61.9	63.6±3.3	6.3±0.3
	(UV)	(83.3)	(92±13)	(29±8)
$T \rightarrow 2M$	NMR	90.8	84±15	-21±40
	VIS**	84.9	80.8±2.9	-13.4±0.8
	(UV)	(102.1)	(102.5±1.3)	(15.7±0.4)

a) Note: For spectrometric methods the errors reported are those given by least-square fitting, whereas for the NMR data the systematic errors are also included.

b) Values as obtained from $\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$.

c) Values as obtained from $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

From Fig. 4 and Table 3 it seems clear that $\tau_{\bar{C}M}^{-1}$ (from NMR) and τ_{I}^{-1} (from stopped flow) can both be identified as rate constant k_1. This concurs with the experimental findings of the non-observable concentration dependence in τ_I, the term $4k_{-1}\bar{C}_M$ in eqn (4) being small compared to k_1. Likewise, Fig. 5 and Table 3 indicate that $\tau_{\bar{T}M}^{-1}$ (from NMR) and k_{II} (from spectrophotometry) can both be identified with k_2. Indirectly all this may be taken as evidence for the correctness of the mechanism illustrated in Scheme 1a.

DISCUSSION

Kinetic studies concerning the dissociation reaction have been reported, but deal merely with aliphatic and aralkyl azodioxy compounds.[16,17,21–24] Fairly recently, two mechanistic studies on the *cis–trans* isomerization of two aliphatic derivatives, namely azodioxymethane and azodioxycyclohexane, have appeared.[16,17] In these cases, the dissociation reaction is slow enough to be investigated by conventional spectrophotometry. The *cis* and *trans* isomers were available in the crystalline form and made possible the preparation of solutions containing either azodioxy isomer. The investigation of the dynamics was based on difference in the UV absorption spectra of these species. The rearrangement of the nitroso compound into its corresponding oxime seems to have hindered more comprehensive kinetical studies. Gowenlock and Redish showed that special precautions are necessary to make the kinetical studies clearly interpretable.[25]

Wajer and De Boer were able to obtain reasonably reliable data on the kinetics of the *cis–trans* isomerization of azodioxycyclohexane, once they were able to show that this compound undergoes *cis–trans* isomerization exclusively through the monomer at room temperature.[17] It should be remembered that the oxime rearrangement is not possible with the present compound.

For the purpose of comparison, the kinetic parameters obtained in the work of Wajer and De Boer are presented in Table 3 (in parentheses) together with the corresponding parameters obtained by us.

Taking into account structural differences and experimental errors, the entropy value ΔS° for the dissociation reaction is almost the same for azodioxycyclohexane and azodioxytoluene. The activation enthalpies, ΔH^{+}, for the dissociation process of *o,o'*-azodioxytoluene, viz. *cis*→2M and *trans*→2M, are considerably lower than those obtained for azodioxycyclohexane. This kind of difference is probably a distinctive feature between aromatic and aliphatic compounds. Any close comparison with measurements on other compounds is not meaningful since they were not measured in acetonitrile and the activation parameters depend greatly on the solvent used.

Several attempts to describe the mechanism of the dimerization (or dissociation process) in nitroso-azodioxy systems on a more theoretical basis have been made without leading to any definite conclusions. Lüttke has assumed a dimerization-dissociation planar reaction path occurring by a coplanar motion of the two monomers.[7] However, as stressed by Hoffman *et al.*, such a planar process is not probable according to the noncrossing rule.[26] Hence, Hoffman has proposed a non-least motion process not proceeding in a plane. The energy barriers computed for HNO using Extended Hückel Theory were not found to be in accordance with those observed experimentally. In a more recent *ab initio* quantum chemical study, calculations predicted a surprisingly high energy barrier for the dissociation process of 101 kcal/mole.[27] This should be compared with the experimental data of approximately 20 kcal/mole (see Table 2).

It is appropriate to make some comments about the energy barrier of a possible direct *cis–trans* isomerization (though it is not observed) because of the more kinetically probable indirect process proceeding via the monomer.

From crystallographic measurements, the N=N bond lengths are known to decrease to about 1.32, 1.26 and 1.22 Å when going from azodioxy to azo and azoxy compounds respectively.[28–30] Thus, one might expect the NN double bond character to increase as azodioxy < azo < azoxy, and, as a first approximation, any rotational barrier also increases in that order. For aromatic azo and azodioxy compounds, Arrhenius activation energies of 22 och 20 kcal/mole respectively have been experimentally observed.[31,32] However, these values appear to relate to the inversion path, possible in these two latter classes of compounds. In fact, any rotational barrier is expected to be considerably higher.

EXPERIMENTAL

Chemicals. o,o'-Azodioxytoluene was commercial (Aldrich Europe) and purified by sublimation (at least 99% purity as checked by mass spectrometry). *Cis* and *trans* crystals were prepared and identified according to procedures described earlier.[18] Spectroscopic grade acetonitrile available commercially from Merck has been used without further purification and dried with molecular sieves in all the experimental work involving optical detection of the monomeric species. Deuterated solvents, CD_3CN and $CDCl_3$, were purchased from CIBA and used in the NMR investigation.

Spectroscopic studies. All the spectrophotometric measurements were carried out on a Shimadzu MPS-50L double beam spectrophotometer. At temps below room temp, the spectrophotometer was purged continuously with N_2 or dry air. The cell holders were thermostated by circulating EtOH from a constant temp bath. The temp of the solns was measured continuously by means of a copper-constantan thermocouple connected to a digital voltmeter. The temps could be kept constant within ±0.2°.

Measurements were made of the overall equilibrium of the dimer $\rightleftarrows$ monomer equilibrium on recordings of the monomer spectrum in the wavelength region 425–825 nm, concentration range $2.0\times10^{-3}-2.5\times10^{-1}$ M. Samples were prepared immediately *prior* to the experiments by weighing *o,o'*-azodioxytoluene together with the solvent (*ca.* 21 ml or 50 ml) in E-flasks.

The equilibration measurements were carried out with a 1 cm cell (*ca.* 3 ml) with the addition of 10 mg of *o,o'*-azodioxytoluene in a pre-thermostated cell which was vigorously shaken (2–3 sec). In the rapid-dilution experiments, an Oxford rapid-dispensing syringe equipped with polyethene tips of 50μl-size was used. The agitation following the injection was sufficiently vigorous in all experiments to yield homogeneous solns. The stopped-flow studies were performed with an Aminco-Morrow unit with effective mixing of equal volumes of water solns in 2–3 msec. For keeping the temp in the cell constant, an external gas stream had to be employed in addition to internal thermostating of mixing chamber. Continuous monitoring of the temps was carried out with thermocouples fixed to the sides of the cell. In all kinetic experiments the absorption of the monomer was followed.

NMR spectra. These were taken on a JEOL MH-100 spectrometer operating at 100 MHz with internal lock and field sweep. The spectra of the Me protons were recorded at a sweep rate of 0.3 Hz/cm and frequency scale factor 3 Hz/cm. A signal arising from a small amount of impurity (<1%) was used as internal reference. Temp measurements were made by means of a copper-constantan thermocouple fixed in the insert. This thermocouple was calibrated against another thermocouple kept inside a spinning NMR tube. This allows for an accuracy of at least ±0.5°. The NMR equilibration procedures have already been described above.

Acknowledgements—This research was supported by the Swedish Natural Research Council under contract No K 2471. The valuable help of Drs. T. Drakenberg and U. Isacsson in the experimental NMR and stopped-flow studies, respectively, is gratefully acknowledged.

REFERENCES

[1] B. G. Gowenlock and W. Lüttke, *Quart. Rev.* **12**, 321 (1958).
[2] P. A. S. Smith, *The Chemistry of Open Chain Organic Nitrogen Compounds*, Vol. II, Chap. 13. Benjamin, New York (1966).
[3] J. H. Boyer, *The Chemistry of the Nitro and Nitroso Groups* Part I (Edited by H. Feuer) p. 215. Wiley, New York (1968).
[4] S. Darwin and D. C. Hodgkin, *Nature* **166**, 827 (1950).
[5] C. P. Fenimore, *J. Am. Chem. Soc.* **72**, 3226 (1950).
[6] K. Nakamoto and R. E. Rundle, *Ibid.* 1113 (1956).
[7] W. Lüttke, Habilitationsschrift, Freiburg i. Br. (1956).
[8] C. Rømming and H. J. Talberg, *Acta Chem. Scand.* **27**, 2246 (1973).
[9] D. A. Dieterich, I. C. Paul and D. Y. Curtin, *J. Am. Chem. Soc.* **96**, 6372 (1974).
[10] C. K. Prout, A. Coda, R. A. Forder and B. Kamerar, *Cryst. Struct. Comm.* **3**, 39 (1974).
[11] C. K. Ingold and H. A. Piggott, *J. Chem. Soc.* **125**, 169 (1924).
[12] D. L. Hammick, *Ibid.* **134**, 3105 (1931).
[13] W. J. Mijs, S. E. Hoekstra, R. H. Ullman and E. Havinga, *Rec. Trav. Chim.* **77**, 746 (1958).
[14] B. G. Gowenlock and J. Trotman, *J. Chem. Soc.* 4190 (1955).
[15] B. G. Gowenlock and J. Trotman, *Ibid.* 1670 (1956).
[16] A. U. Chaudhry and B. G. Gowenlock, *Ibid.* (B) 1083 (1968).
[17] Th. A. J. W. Wajer and Th. J. DeBoer, *Recueil* **91**, 565 (1972).
[18] M. Azoulay, B. Stymne and G. Wettermark, *Tetrahedron* **32**, 2961 (1976).
[19] M. Azoulay, T. Drakenberg and G. Wettermark, *Tetrahedron Letters* No. **26**, 2243 (1974).
[20] H. M. McConnell, *J. Chem. Phys.* **28**, 430 (1958).
[21] L. Batt and B. G. Gowenlock, *Trans. Far. Soc.* **56**, 1022 (1960).
[22] L. Batt and B. G. Gowenlock, *J. Chem. Soc.* 376 (1960).
[23] B. G. Gowenlock and J. Kay, *Ibid.* 2880 (1962).
[24] J. R. Schwartz, *J. Am. Chem. Soc.* **79**, 4353 (1957).
[25] B. G. Gowenlock and K. A. Redish, *Z. Phys. Chem. NF* **31**, 169 (1962).
[26] R. Hoffmann, R. Gleiter and F. B. Mallory, *J. Am. Chem. Soc.* **92**, 1460 (1970).
[27] A. B. Heiberg and H. J. Talberg, private communication.
[28] A. Mostad and C. Rømming, *Acta Chem. Scand.* **25**, 3561 (1971).
[29] D. A. Dieterich, I. C. Paul and D. Y. Curtin, *J. Am. Chem. Soc.* **96**, 6372 (1974).
[30] W. R. Krigbaum, Y. Chatani and P. G. Barber, *Acta Crystallogr.* **B26**, 97 (1970).
[31] S.-B. Rhee and H. H. Jaffé, *J. Am. Chem. Soc.* **95**, 5518 (1973).
[32] E. V. Brown and G. R. Granneman, *Ibid.* **97**, 621 (1975).