AROMATIC C-NITROSO COMPOUNDS. NMR STUDIES ON THE

INTERNAL ROTATION AND *CIS-TRANS* ISOMERIZATION OF

DIMERIC o-NITROSOTOLUENE

Michel Azoulay[*], Torbjörn Drakenberg[**] and Gunnar Wettermark[*]

[*]Division of Physical Chemistry, The Royal Institute of Technology,

S-100 44 Stockholm 70, Sweden

[**]Division of Physical Chemistry, The Lund Institute of Technology,

Chemical Center, P.O.Box 740, S-220 07 Lund 7, Sweden

C-nitroso compounds are of considerable interest in chemistry because of dimerization and *cis-trans* isomerization of the dimer. The dimer formation has been the subject of extensive discussions in the literature[1-14]. A pronounced *ortho*-effect is present in aromatic compounds. Ultraviolet and visible, infrared and NMR spectroscopy have been widely applied to obtain qualitative informations on a variety of primary, secondary and tertiary alkyl, cycloaliphatic, aralkyl and aromatic nitroso compounds. Concerning quantitative studies, conventional ultraviolet and visible spectrophotometry has proven very useful in determining the dissociation rates of non aromatic compounds, as well as the equilibrium constants of the dimer-monomer equilibrium. The matter is covered in several reviews[15-17]. However, to our knowledge, no equilibrium studies and kinetic investigations of the *cis-trans* isomerization of aromatic nitroso compounds have been reported.

In the present communication we wish to report NMR observations of two hitherto unknown kinds of exchange processes present in the aromatic nitroso compound o-nitrosotoluene. We believe that one of these exchanges is related to the *cis-trans* isomerization while the other is due to rotational isomerism.

in the dimer (rotation about an "essential single bond"). Moreover, preliminary investigations show that both of these problems are amenable to the NMR line-shape method.

o-Nitrosotoluene is known to exist, like most aromatic C-nitroso compounds, as a *trans* dimer in the solid state and to dissociate readily to two monomers in various organic solvents at room temperature[1,18-20]. In contrast to many aliphatic nitroso compounds studies of the temperature dependence of the dimer/monomer equilibrium show that this dissociation reaction is reversible. Although it has been established that the NMR spectrum of the methyl protons consists of two signals due to the monomer and the dimer respectively, it has not been known that the dimer signal is indeed a doublet (figure 1 c) and at lower temperatures a triplet (figure 1 a).

Both signals of the doublet, designated T and C, decrease with increasing temperature. Above +20°C, in CD_3CN, broadening due to an exchange process between the T and monomer signals becomes more and more pronounced. At temperatures higher than 40°C the same effect is also operating for the C and monomer signals. Above 75°C the dimer and monomer signals have collapsed into one. It is noteworthy to report that no direct exchange between the doublet signals is observed.

At temperatures below 0°C the signal T is broadened and at -50°C it is split into two well separated signals T_A and T_B (figure 1 a).
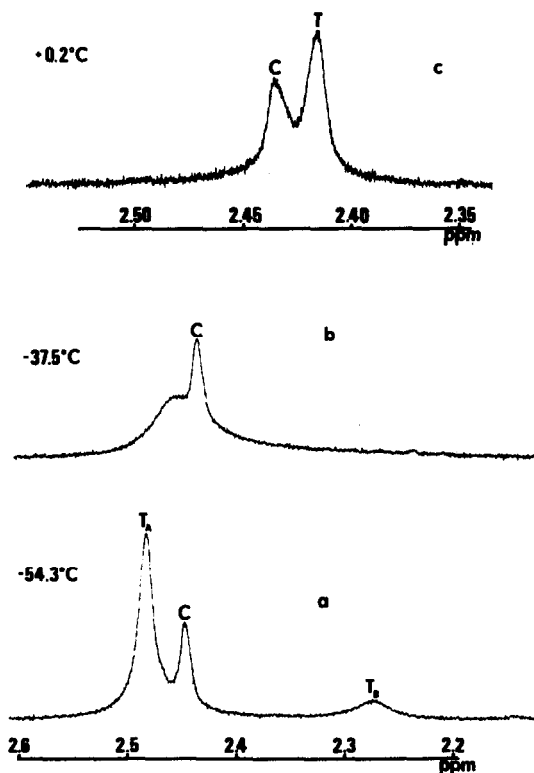

Fig. 1. 100 MHz NMR spectrum of the methyl protons of dimeric o-nitroso-toluene at various temperatures. The monomer signal is located at about 3.2 ppm (reference TMS, solvent CH_2Cl_2).

Although the assignment of the three different signals shown in figure 1 is not quite straightforward, the observed exchange processes may in a consistent way be correlated to the following chemical reactions (where $(RNO)_2$ stands for the dimeric o-nitrosotoluene):

1. Temperature range 20° - 75°C.
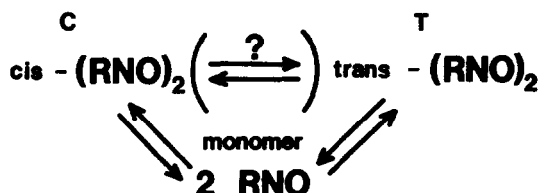
A similar reaction scheme has been formulated already for aliphatic nitroso compounds, and recently Wajer and De Boer have shown that their dimers isomerize *cis* ⇄ *trans* exclusively via the monomer.[21,22].

2. Temperature range -60° - 0°C.
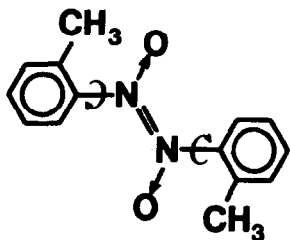
trans - $(RNO)_2$

Rotational isomerism about the C-N bonds in the *trans* dimer as indicated by the arrows in the figure. Pertinent values for the kinetics of this rotational isomerism have been estimated by the NMR line-shape method and some of the results are presented together with equilibrium constants for the *trans* ⇄ *cis* reaction Table 1.

Table 1.

Temp °C	$\Delta G^{\ddagger}$ kcal/mole	ΔG^{O} kcal/mole	$K = \frac{[C]}{[T]}$
-54.3	12.5	0.66	0.22
-37.5	12.4	0.65	0.31

$\Delta G^{\ddagger}$, the free energy of activation, is related to the reaction $T_A \rightarrow T_B$ while ΔG^{O} is the free energy of the equilibrium $T_A \rightleftarrows T_B$. K is the equilibrium constant for the T⇄C reaction as obtained from an analysis of the line-shape of the signals C and T, respectively.

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The two kinds of exchange processes do not interfere and can be treated independently by the NMR line-shape method. Currently we carry out detailed kinetic and mechanistic studies along these lines. Since these reversible processes fall in the NMR time-scale, suitable chemical relaxation methods may also provide a useful tool in studying the kinetics of aromatic C-nitroso compounds. Some steps in the direction of such studies have already been taken in our laboratories. We hope to report in the near future the results of these studies.

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