N-Methyl-1,3,5,2-trioxazinane, a possible spontaneous ignition sensitiser[†]

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_N_-Methyl-1,3,5,2-trioxazinane (or _N_-methyl-2,4,6-trioxapiperidine), by analogy with _s_-trioxane, should decompose thermally into MeNO + 2CH$_2$O; this substance does not appear to have been made, but molecular orbital calculations show that it should be almost as stable as _s_-trioxane.

Nitrogen dioxide, from the thermal decomposition of alkyl nitrates, sensitises the spontaneous ignition of fuel in a diesel engine;[1] likewise, so does formaldehyde, from the thermal decomposition of *s*-trioxane.[2] Synergy occurs between CH_2O and NO_2, so that if both are released simultaneously, the ignition quality of the fuel is even more enhanced. The efficiency of 2-ethylhexyl nitrate as a sensitiser of diesel-fuel ignition arises because following its dissociation into NO_2 and an alkoxy radical, a fraction[3] of these radicals goes on to eliminate CH_2O. However, with increasing legislative pressure to minimise NO_x emissions,[4] strategies for increasing the ratio of CH_2O/NO_2 formation could be beneficial.

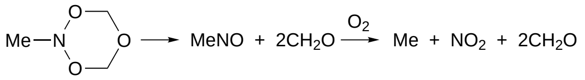
An obvious choice is the thermal decomposition of phenethyl nitrate [eqn. (1)], not only giving the desired

$$\begin{aligned} \mathrm{PhCH_2CH_2ONO_2} &\rightarrow \mathrm{PhCH_2CH_2O} + \\ \mathrm{NO_2} &\rightarrow \mathrm{PhCH_2} + \mathrm{CH_2O} + \mathrm{NO_2} \end{aligned} \tag{1}$$

products in equal amounts, but yielding also benzyl radicals, which are powerful ignition sensitisers.[5] The hoped-for advantage, however, does not materialise in engine measurements[6] because in the temperature range of interest (*ca.* 650–800 K), phenethyl nitrate[7] decomposes an order of magnitude more slowly than does 2-ethylhexyl nitrate[3a]

$$\text{(phenethyl nitrate: } k = 5.0 \times 10^{13} e^{-35{,}600/1.987T}\ \mathrm{s}^{-1}\text{;}$$
$$\text{2-ethylhexyl nitrate: } k = 2.5 \times 10^{15} e^{-37{,}500/1.987T}\ \mathrm{s}^{-1}\text{).}$$

N-Methyl-1,3,5,2-trioxazinane, by analogy with the thermal decomposition of *s*-trioxane into three CH_2O molecules (or other symmetrically substituted alkyltrioxanes into three aldehyde molecules),[8] should yield two CH_2O molecules and MeNO, the latter decomposing rapidly to give NO and thence NO_2 in the presence of excess oxygen [eqn. (2)].



(2)

Thus, we explored a parallel set of GAUSSIAN 94 molecular orbital calculations[9] for these two molecules. Their equilibrium geometries were found at the RHF/6-31G** level of theory, as were the transition states for the concerted dissociations [eqns. (3) and (4)], with key energies further

$$(\mathrm{CH_2O})_3 \rightarrow 3\mathrm{CH_2O} \tag{3}$$

$$\mathrm{MeNO(CH_2O)_2} \rightarrow \mathrm{MeNO} + 2\mathrm{CH_2O} \tag{4}$$

refined at the MP2 and/or MP4 levels. All characteristic structures were verified by harmonic vibration analysis, and by demonstrating that equivalent structures could be found by non-local density functional calculations; in the case of *s*-trioxane, all of the reported structures were duplicated with both the B3LYP and BHandHLYP functionals, but for brevity only the latter results are presented. Also, for the *N*-methyl-1,3,5,2-trioxazinane molecule, because of its increased size and complexity, slightly less demanding levels of approximation were used, and extensive searches were made for both singlet and triplet configurations to eliminate the possibility of a lower energy path for the breakup or structural rearrangement. The results of these calculations are collected together in Tables 1 and 2.

For *s*-trioxane, the minimum energy configuration is, as expected, in the chair form, with C–O and C–H bond lengths each within 1% of 1.40 and 1.08 Å, respectively, in all levels of approximation. Also, there is always a local minimum for the $(CH_2O)_2$ configuration, with bond lengths approximately 1% longer than in *s*-trioxane. The transition state for the dissociation was characterised by an imaginary vibrational degree of freedom which corresponds precisely to a concerted dissociation into three CH_2O molecules. At the energy maximum, the C–O bonds now alternate between 1.25 and 1.90 Å in length, compared with the calculated C–O distance in formaldehyde itself of *ca.* 1.20 Å. Concerted dissociations of six-membered ring compounds into three identical fragments, *viz.* 1,3,5-triaza-

Table 1 RHF/6-31G** energies for the reaction systems $(CH_2O)_3 \rightarrow 3CH_2O$ and $MeNO(CH_2O)_2 \rightarrow MeNO + 2CH_2O$

System[a]	Symmetry	*E*/a.u.[b]	zpe/a.u.[b]
CH_2O	C_{2v}	−113.8697	0.0290
$(CH_2O)_2$	D_{2h}	−227.7374	0.0689
‡$(CH_2O)_3$	C_3	−341.5580	0.0989
$(CH_2O)_3$	C_{3v}	−341.6649	0.1079
MeNO	C_s	−168.8344	0.0471
‡$MeNO(CH_2O)_2$	C_s	−396.5941	0.1242
$MeNO(CH_2O)_2$	C_1	−396.5021	0.1163

[a] ‡ Signifies the transition state. [b] 1 a.u. = $2I_H$ = 27.2 eV = 627.5 kcal mol^{-1} = 2625.5 kJ mol^{-1}.

Table 2 Density functional, MP2 and MP4 estimates of energy differences in the $(CH_2O)_3$ and $MeNO(CH_2O)_2$ reaction systems

System[a]	*E*/a.u.[b]	zpe/a.u.[b]	ΔE_0/a.u.[b]
BHandHLYP/6-311+G**			
$3CH_2O$	−343.4202	0.0828	+0.0434 (+27)
‡$(CH_2O)_3$	−343.3937	0.0944	+0.0815 (+51)
$(CH_2O)_3$	−343.4841	0.1033	0
BHandHLYP/6-311G*			
MeNO + $2CH_2O$	−398.6663	0.1008	+0.0206 (+13)
‡$MeNO(CH_2O)_2$	−398.6392	0.1195	+0.0664 (+42)
$MeNO(CH_2O)_2$	−398.6981	0.1120	0
RMP2/6-31G**//RHF/6-31G**			
‡$(CH_2O)_3$	−342.5221	0.0989	+0.0783 (+49)
$(CH_2O)_3$	−342.6094	0.1079	0
‡$MeNO(CH_2O)_2$	−397.6463	0.1242	+0.0619 (+39)
$MeNO(CH_2O)_2$	−397.7161	0.1163	0
RMP4/6-311G**//RHF/6-31G**			
‡$(CH_2O)_3$	−342.7541	0.0989	+0.0717 (+45)
$(CH_2O)_3$	−342.8348	0.1079	0

[a] ‡ Signifies the transition state. [b] 1 a.u. = $2I_H$ = 27.2 eV = 627.5 kcal mol^{-1} = 2625.5 kJ mol^{-1}. Figures in parentheses in kcal mol^{-1}.

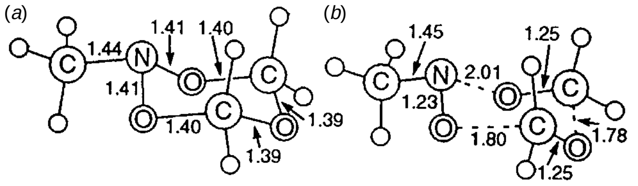


Fig. 1 Structures of (*a*) the lowest energy conformer of *N*-methyl-1,3,5,4-trioxazinane and (*b*) the transition state for dissociation. Distances are in Å.

cyclohexane $\rightarrow$ $3H_2C{=}NH$, trinitro-1,3,5-triazacyclohexane $\rightarrow$ $3H_2C{=}N{-}NO_2$ and *sym*-triazine $\rightarrow$ 3HCN, have been studied previously by molecular orbital methods.[10]

The thermochemical results for dissociation into three CH_2O molecules are typical of what one can expect at the present time for a reaction with unequal numbers of reactants and products. The latest thermochemical data for *s*-trioxane[11] and for formaldehyde[12] give $\Delta H_{298} \simeq +33$ kcal mol^{-1}, or about +30 kcal mol^{-1} at 0 K; an alternative datum for formaldehyde[13] gives values of +28 and +25 kcal mol^{-1} respectively. The results for 0 K from these calculations are +22, +27, +28 and +20 kcal mol^{-1} from the RHF, DFT, MP2 and MP4 calculations respectively; unscaled zero point energies (zpe) are used in all calculations.

For *N*-methyl-1,3,5,2-trioxazinane there are six conformers, with the one of lowest energy being again in a chair configuration; we did not examine the other five structures beyond RHF/6-31G**. Again, all the C–H distances are about 1.08–1.09 Å and the lowest path to dissociation is a concerted one, but the structure of the transition state is slightly asymmetric; the two structures are shown in Fig. 1. Comparison of the energies given in Table 2 would suggest that both the enthalpy and activation energy for the dissociation into three fragments are about 10 kcal mol^{-1} less for this molecule than for *s*-trioxane.

There have been several kinetic studies of the thermal decomposition of *s*-trioxane: in the 500–800 K temperature range, three conventional studies[14] all gave activation energies of between 47–48 kcal mol^{-1}, and frequency factors of $10^{14.80}$ to $10^{15.28}$ s^{-1}; in addition, a high-temperature shock tube study[15] gives results that extrapolate nicely into this body of measurements. By comparison, our MP2 and MP4 results for the activation energy at 0 K are 49 and 45 kcal mol^{-1} respectively.

A straightforward transition state calculation[16] of the rate constant for the thermal dissociation of *s*-trioxane over the temperature range 500–800 K yields an Arrhenius *A* factor of $10^{15.56}$ s^{-1}, and an activation energy of 52.1 or 48.1 kcal mol^{-1}, depending upon which value of the critical energy is used.¶ These results compare favourably with the experimental ones quoted above.

Likewise, for *N*-methyl-1,3,5,2-trioxazinane decomposing into $2CH_2O$ + MeNO, we find an Arrhenius *A* factor of $10^{15.25}$ s^{-1}, and an activation energy of 41.7 kcal mol^{-1}, using the frequency data and the MP2 result for the critical energy of activation.¶ These rate parameters are rather similar to those for 2-ethylhexyl nitrate, noted above, making this new substance an ideal candidate for a diesel-fuel ignition sensitiser.

The close parallels between the various structures in the two systems, and moderate acceptability of the *s*-trioxane results (both for the thermochemistry and the reaction rate), tend to suggest that the calculations on *N*-methyl-1,3,5,2-trioxazinane can be accepted with a reasonable degree of confidence. Thus, *N*-methyl-1,3,5,2-trioxazinane should be a stable molecule, with an activation energy for concerted dissociation into nitrosomethane and formaldehyde in the region of 35–40 kcal mol^{-1}. In which case, it may seem surprising that this heterocycle has apparently never been reported, particularly since quite a number of examples of *N*,*N*-dialkoxy-*N*-alkylamines or *N*,*N*-dialkoxybenzamides are known.[17]

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Notes and References

† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://rsc.org/ccenhanced

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¶ The following are the vibrational and rotational constants, at the DFT-RHF/6-311G* level of approximation, used in the transition state calculations; vibrational degeneracies, if any, are in parentheses.

s-Trioxane, ground state: vibration: 298(2), 468, 555(2), 803, 1009(2), 1033, 1059, 1130(2), 1265(2), 1295, 1309, 1390(2), 1460, 1504(2), 1566(2), 1585, 3041(2), 3058, 3245(2), 3248 cm^{-1}; rotation: 0.1793, 0.1793, 0.09938 cm^{-1}.

s-Trioxane, transition state: vibration: 176(2), 276(2), 315, 461(2), 547, 911, 943(2), 1178, 1278(2), 1289, 1290(2), 1473, 1511(2), 1644, 1691(2), 3071(2), 3072, 3210(2), 3212 cm^{-1}; rotation: 0.1451, 0.1451, 0.07979 cm^{-1}.

N-Methyl-1,3,5,2-trioxazinane, ground state: vibration: 192, 251, 345, 371, 398, 512, 594, 618, 821, 888, 900, 1024, 1050, 1145, 1146, 1203, 1219, 1239, 1275, 1320, 1360, 1406, 1479, 1505, 1519, 1547, 1560, 1564, 1582, 3112, 3120, 3142, 3231, 3259, 3263, 3265 cm^{-1}; rotation: 0.1777, 0.09097, 0.06509 cm^{-1}.

N-Methyl-1,3,5,2-trioxazinane, transition state: vibration: 149, 189, 213, 253, 280, 307, 341, 488, 517, 589, 629, 975, 1036, 1067, 1141, 1214, 1257, 1290, 1309, 1347, 1456, 1474, 1493, 1504, 1546, 1550, 1639, 1667, 3066, 3114, 3138, 3177, 3226, 3227, 3286 cm^{-1}; rotation: 0.1429, 0.08135, 0.05610 cm^{-1}.

1 P. Q. E. Clothier, B. D. Aguda, A. Moise and H. O. Pritchard, *Chem. Soc. Rev.*, 1993, **22**, 101.
2 P. Q. E. Clothier, H. O. Pritchard and M.-A. Poirier, *Combust. Flame*, 1993, **95**, 427.
3 (*a*) H. O. Pritchard, *Combust. Flame*, 1989, **75**, 415; (*b*) M. A. R. Al-Rubaie, J. F. Griffiths and C. G. W. Sheppard, *Some observations on the effectiveness of additives for reducing the ignition delay period of diesel fuels*, SAE Technical Paper Series, 1991, 912333.
4 G. Baumbach, *Air Quality Control*, Springer, Berlin, 1996, ch. 2, 7 and 8.
5 P. Q. E. Clothier, D. Shen and H. O. Pritchard, *Combust. Flame*, 1995, **101**, 383.
6 P. Q. E. Clothier and H. O. Pritchard, unpublished work.
7 M. A. Hiskey, K. R. Brower and J. C. Oxley, *J. Phys. Chem.*, 1991, **95**, 3955.
8 C. C. Coffin, *Can. J. Res. (B)*, 1932, **7**, 75; 1933, **9**, 603.
9 See M. J. Frisch, A. Frisch and J. B. Foresman, *GAUSSIAN 94 User's Reference*, Gaussian, Inc., Pittsburgh PA, 1996, p. 2, for complete citation.
10 D. Habibollahzadeh, M. Grodzicki, J. M. Seminario and P. Politzer, *J. Phys. Chem.*, 1991, **95**, 7699; S. V. Pai, C. F. Chabalowski and B. M. Rice, *ibid.*, 1996, **100**, 15 368.
11 M. Mansson, E. Morowetz, Y. Nakase and S. Sunner, *Acta Chem. Scand.*, 1969, **23**, 15.
12 R. A. Fletcher and G. Pilcher, *Trans. Faraday Soc.*, 1970, **66**, 794.
13 *JANAF Thermochemical Tables*, 2nd edn., NSRDS-NBS 37, National Bureau of Standards, Washington, D.C., 1971.
14 R. Le G. Burnett and R. P. Bell, *Trans. Faraday Soc.*, 1938, **34**, 420; W. Hogg, D. M. McKinnon, A. F. Trotman-Dickenson and G. J. O. Verbeke, *J. Chem. Soc.*, 1961, 1403; S. Hochgreb and F. L. Dryer, *J. Phys. Chem.*, 1992, **96**, 295.
15 E. A. Irdam and J. H. Kiefer, *Chem. Phys. Lett.*, 1990, **166**, 491.
16 S. Glasstone, K. J. Laidler and H. Eyring, *The theory of rate processes*, McGraw-Hill, New York, 1941, p. 192.
17 V. F. Rudchenko, S. M. Ignatov and R. G. Kostyanovskii, *J. Chem. Soc., Chem. Commun.*, 1990, 261; J. J. Campbell and S. Glover, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1661 and references cited therein.

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