Thermal Isomerization of Benzene *cis*-Trioxide (3,6,9-Trioxatetracyclo-[6.1.0.0^{2,4}.0^{5,7}]nonane)

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Benzene *cis*-trioxide has been pyrolysed in the gas phase in the temperature range 475—537 K. Only one product, all-*cis*-1,4,7-trioxacyclononatriene, was observed. First-order rate constants taken from the upper part of this range (515—537 K) fit the Arrhenius equation (i). The reaction is probably unimolecular and a detailed mechanism is discussed.

$$\log_{10}(k/\mathrm{s}^{-1}) = 14.9 \pm 0.6 - (176\ 900 \pm 6\ 200\ \mathrm{J\ mol}^{-1})/RT\ln 10 \qquad \text{(i)}$$

THE thermal isomerization of a number of saturated compounds containing one epoxide group have been reported.[1-8] In these cases, unsaturated ether formation, when observed, results from fission of the C–C bond of the epoxide ring and a 1,4-hydrogen transfer. In two cases [5,8] the observed *cis* : *trans* product ratios suggested the intermediacy of a $>\dot{\mathrm{C}}\mathrm{O}\dot{\mathrm{C}}<$ diradical, although such a mechanism is difficult to reconcile with the energetics of these systems. In 1,2-epoxybutane, for example, the activation energy for the formation of methyl propenyl ether is 227 kJ mol^{-1} whereas the $\Delta H_f°$ difference between the $>\dot{\mathrm{C}}\mathrm{O}\dot{\mathrm{C}}<$ diradical and 1,2-epoxybutane, calculated by group additivity procedures [9] is 223 kJ mol^{-1}. This implies, if hydrogen transfer is rate determining, an activation energy for the 1,4-hydrogen transfer of 4 kJ mol^{-1}, which is an unreasonably low value. An estimate can be made which puts E_a for such a step at >50

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[1] (*a*) W. W. Heckert and E. Mack, *J. Amer. Chem. Soc.*, 1929, **51**, 2706; (*b*) C. J. M. Fletcher and G. K. Rollefson, *ibid.*, 1936, **58**, 2135; (*c*) K. H. Mueller and W. D. Walters, *ibid.*, 1951, **73**, 1458; 1954, **76**, 330; (*d*) M. L. Neufeld and A. T. Blades, *Canad. J. Chem.*, 1963, **41**, 2956.

[2] (*a*) A. T. Blades, *Canad. J. Chem.*, 1968, **46**, 3283; (*b*) T. J. Hardwick, *ibid.*, p. 2454.

[3] M. C. Flowers, R. M. Parker, and M. A. Voisey, *J. Chem. Soc.* (*B*), 1970, 239.

[4] M. C. Flowers and R. M. Parker, *Internat. J. Chem. Kinetics*, 1971, **3**, 443.

[5] M. C. Flowers and R. M. Parker, *J. Chem. Soc.* (*B*), 1971, 1980.

[6] M. C. Flowers, D. E. Penny, and J.-C. Pommelet, *Internat. J. Chem. Kinetics*, 1973, **5**, 353.

[7] M. C. Flowers and D. E. Penny, *J.C.S. Faraday I*, 1974, 355.

[8] M. C. Flowers and D. E. Penny, *J.C.S. Faraday I*, 1975, 851.

[9] (*a*) S. W. Benson, ' Thermochemical Kinetics,' Wiley, New York, 1968; H. E. O'Neal and S. W. Benson, (*b*) *J. Phys. Chem.*, 1968, **72**, 1866; (*c*) *Internat. J. Chem. Kinetics*, 1969, **1**, 221; (*d*) *ibid.*, 1970, **2**, 423.

kJ mol^{-1}.[10] This suggests that either the process is concerted or that the $>\dot{C}O\dot{C}<$ diradical enjoys a degree of stabilization unaccounted for in the group additivity calculations. In the isomerization of *trans*-1,2-divinyloxiran to 2-vinyl-2,3-dihydrofuran,[11] however, where no hydrogen transfer step is required, the activation energy can be accounted for by considering the allylic stabilization of the diradical. No hydrogen transfer step is required for ether formation in the present study, and the process is orbital symmetry allowed; hence the Arrhenius parameters should be of interest.

EXPERIMENTAL AND RESULTS

Benzene *cis*-trioxide (3,6,9-trioxatetracyclo[6.1.0.$0^{2,4}$.$0^{5,7}$]-nonane) whose isomerization to a cyclic ether has been reported,[12] is a crystalline solid, m.p. 242°.* Pyrolyses were effected therefore by immersing glass ampoules, containing the trioxide, in a fused salt (KNO_3–$NaNO_2$ binary eutectic) thermostat. The ampoules (*ca.* 8 cm in length, 6 mm i.d.) were prepared by attaching glass tubes, containing the trioxide in methylene chloride solution, to a vacuum system and, after flash evaporation of the solvent, sealing them with a small flame. Each tube contained *ca.* 10^{-5} mol of trioxide which, given the above ampoule dimensions, would have produced a pressure of *ca.* 100 Torr (1 Torr ≡ 133 N m^{-2}), assuming complete vaporization.

Some tubes were rinsed with ammonium hydroxide prior to use but this appeared to have no effect on the reaction rate. After pyrolysis the contents of each ampoule were diluted with toluene prior to injection onto the gas chromatograph, the toluene acting both as a diluent and an internal standard. The analysis was with a 4 m × $\frac{1}{8}$ in o.d. silicone oil column held at 150° in a Perkin-Elmer F11 chromatographic oven. Detection was by flame ionization and peak areas were obtained using a Hewlett–Packard 3371B integrator.

Only one pyrolysis product was observed, whose n.m.r. spectrum corresponded to all-*cis*-1,4,7-trioxacyclononatriene.[12] As expected the trioxide itself did not elute from the chromatographic column and hence the initial concentration of reactant (a_0) could not be obtained in the conventional way of totalling the integrated areas of reactant and product peaks.

A plot of ln $[a_0/(a_0 - x)]$ against time, however, should, if the isomerization is subject to a first-order rate law, be linear and should pass through the origin. By using a series of ampoules, therefore, containing equal amounts of trioxide and employing the values of x (integrated product peaks) obtained at different pyrolysis times, a value of a_0 could be deduced which resulted in a zero intercept for the first-order rate plot.

It was found that such plots were linear for up to 50% decomposition, after which the plots began to turn over, possibly as a result of a secondary dimerization reaction. The value of a_0 found at the first temperature (525 K) was used at all subsequent temperatures with suitable corrections for variations in the sample size.

After the initial first-order dependence had been established, it was decided, in an attempt to limit the necessarily tedious procedure of ampoule preparation, to carry out at each temperature, kinetic runs for such time that the total conversion was *ca.* 30%. This extent of reaction being chosen so that first-order behaviour was assured and that good analytical precision could be achieved. Three runs, each being analysed at least three times, were carried out at each of 11 temperatures between 475 and 537 K. Averaged rate constants for these runs are given in Table 1. The reproducibility of rate constants was better than 10%.

TABLE 1

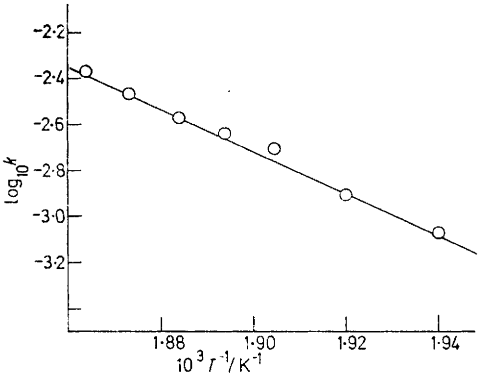
First-order rate constants for the decomposition of benzene *cis*-trioxide

T/K	$10^5k/s^{-1}$	T/K	$10^5k/s^{-1}$
475.0	0.924	525.1	195
485.7	3.10	528.1	227
495.4	10.6	530.8	267
505.8	28.0	533.9	339
515.5	84.0	536.5	432
520.8	122		

When represented on an Arrhenius plot (Figure) only points corresponding to temperatures in excess of 515 K fall on a good straight line, a least squares treatment of which yields equation (1). The errors quoted are standard

$$k/s^{-1} = 10^{14.9 \pm 0.6} \exp(-176\,900 \pm 6\,200 \text{ J mol}^{-1}/RT) \quad (1)$$

deviations which although large are felt to be reasonable in view of the technique employed and the limited temperature range.



Arrhenius plot for benzene *cis*-trioxide

Deviations from the Arrhenius line at temperatures below 515 K (the reported [12] m.p.) are probably due to increasing overestimations of the true value of a_0, because of surface effects, including incomplete vaporization of the benzene trioxide. A conventional packed vessel test was not possible in view of the amounts of material involved and the technique of extracting samples for chromatographic analysis. By using different diameter tubing, however, the surface: volume ratio was changed by a factor of two, without any significant alteration in the rate.

DISCUSSION

The isomerization is an orbital symmetry allowed $[_{\sigma}2_s + _{\sigma}2_s + _{\sigma}2_s]$ cycloreversion, which according to

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* Thanks are expressed to Professor Dr. H. Prinzbach, University of Freiburg, for a sample of benzene *cis*-trioxide.

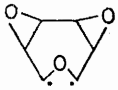
[10] M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1959, 3953.

[11] (*a*) E. Vogel and H. Günther, *Angew. Chem. Internat. Edn.*, 1967, **6**, 385; (*b*) R. J. Crawford, V. Vukov, and H. Tokunaga, *Canad. J. Chem.*, 1973, **51**, 3718.

[12] E. Vogel, H.-J. Altenbach, and C.-D. Sommerfeld, *Angew. Chem. Internat. Edn.*, 1972, **11**, 939.

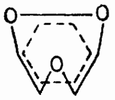
Woodward and Hoffmann[13] can occur by inward disrotatory motions at the termini of the breaking σ bonds.

A diradical mechanism would appear to be ruled out since the initial step would be ring opening to (I). The estimated heat of formation difference between this diradical and benzene trioxide is 240 kJ mol^{-1} whereas the observed E_a is 177 kJ mol^{-1}. There will be some uncertainty attached to this estimate because of the lack of information concerning ring strain contributions, but probably not of the order of 60 kJ mol^{-1}.



(I)

Are the observed Arrhenius parameters consistent with a concerted mechanism? From the value of the pre-exponential factor ($\log_{10} A = 14.9$ s^{-1}) $\Delta S^{\ddagger}$ *ca.* 25 J K^{-1} mol^{-1} (entropy of activation).

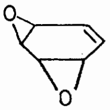


(II)

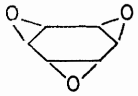
In going to the transition state (II) three of the six σ bonds are elongated and three are shortened, which will probably lead to an increase in entropy. In addition frequencies associated with the oxiran and cyclohexane rings, which are already low, will be lowered even further so that the required $\Delta S^{\ddagger}$ can easily be encompassed.*

Low values of activation energies in concerted processes are associated with energetic assistance during the bond breaking step. In the present case this assistance arises from *p* orbital overlap in double bond formation. The extent of this overlap in the transition state will clearly have a bearing on the value of E_a.

It is interesting to note that the *anti*-isomers of both benzene di- and tri-oxides (III) and (IV), are considerably more stable, with respect to isomerization, than the corresponding *cis*(*syn*)-isomers, even though the isomerizations are still symmetry allowed. Steric interference between an oxygen atom and the six-membered ring during the ring opening process results in relatively high activation energies.[12,14]



(III)



(IV)

TABLE 2

Arrhenius parameters for the isomerization of benzene oxides

	E_a/kJ mol^{-1}	$\log_{10}$ (A/s^{-1})	Ref.
Mono-oxide	38.1 ± 3.3	14.4 ± 1.1	11*a*
Dioxide	133	13.9	*a*
Trioxide	177 ± 6	14.9 ± 0.6	This work

[a] H.-J. Altenbach and E. Vogel, *Angew. Chem. Internat. Edn.*, 1972, **11**, 937.

The Arrhenius parameters for the benzene mono- and di-oxides have been reported and are shown in Table 2. A clear trend in the activation energies is evident. The value of $\Delta S°$ [$S°$ (oxepin) − $S°$(benzene oxide)] quoted by Vogel, as derived from the temperature dependence of the equilibrium constant of 46 J K^{-1} mol^{-1} seems high, and if a more realistic value of *ca.* 6 J K^{-1} mol^{-1} (the estimated $\Delta S°$ for cycloheptatiene and bicyclo[4,1,0]hepta-2,4-diene[15]) were employed, then the A factor would be reduced to *ca.* 10^{13} and a trend in A factors would also be in evidence.

Qualitatively the trend in activation energies can be explained by considering the relative orientation of the *p*-orbitals, required for π bonding in the products, in the benzene oxides. In benzene trioxide all six orbitals are involved in σ bonds in the plane of the cyclohexane ring. To form the product ether, these orbitals must be rotated through 90°. In benzene monoxide, four of the six *p*-orbitals already possess the required orientation of the product and hence favourable overlap in the transition state can be more readily achieved. Benzene dioxide clearly represents an intermediate case.

The trend in the pre-exponential factors, if real, probably results from increasing $\Delta S°$ values as the product rings become larger.

The consequence of this argument for the epoxybutane ismomerizations to unsaturated ethers would be that if, as argued in the introduction, a diradical mechanism is untenable, then the geometry of the transition state in the concerted process, clearly provides poor overlap of the *p*-orbitals required for π bond formation. The transition states, however, are not strictly comparable since, in the epoxybutane case, a hydrogen atom is being transferred and hence it is perhaps not surprising that activation energies *ca.* 40 kJ mol^{-1} higher than reported here for benzene trioxide, are observed.

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* For example each oxiran ring deformation at 900 cm^{-1} becomes a COC bend at 400 cm^{-1} which, at 520 K, produces an increase of entropy of 5 J K^{-1} mol^{-1}.

[13] R. B. Woodward and R. Hoffman, ' The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970.

[14] E. Vogel, H.-J. Altenbach, and E. Schmidbauer, *Angew. Chem. Internat. Edn.*, 1973, **12**, 838.

[15] H. E. O'Neal and S. W. Benson, *J. Chem. and Eng. Data*, 1970, **15**, 266.