Tetrahedron Vol 33, pp 2231 to 2236 Pergamon Press 1977 Printed in Great Britain

THIOCARBONYL AZIDE S-OXIDE—II[1]

THE DECOMPOSITION OF THIOBENZOYLAZIDE S-OXIDE

L. CARLSEN, A. HOLM* and J. P. SNYDER*
Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

and

E. KOCH* and B. STILKERIEG
Institut für Strahlenchemie im Max Planck Institut für Kohlenforschung, D-4330-Mülheim a.d. Ruhr, Stiftstrasse 34-36, Germany

(*Received in the UK* 6 *September* 1976, *Accepted for publication* 24 *January* 1977)

Abstract—The reaction between thiobenzoyl chloride *S*-oxide **4**, (R = C_6H_5) and the azide ion at −80° leads to the labile thiobenzoyl azide *S*-oxide **5**, (R = C_6H_5). Raising the temperature to −40° initiates decomposition of the latter to benzonitrile, nitrogen, sulfur and sulfur dioxide. The thermally induced process was monitored by differential thermal analysis (DTA) which yielded a maximum heat effect at −11°. The derived reaction enthalpy is $\Delta H = -45.6$ kcal mole^{-1} and the activation parameters are $\Delta H^* = 20.2$ kcal mol^{-1}, $\Delta S^* = 6.3$ eu (at −11°). The DTA shape index (S) and the reaction type index (M) are found to be in excellent agreement with a rate controlling first order reaction. Apart from the main peak at −11°, lack of a temperature difference signal throughout the range of measurement rules out an enthalpy-significant azide isomerization and further suggests that decomposition takes place from a single isomer. Semi-empirical energy barrier calculations provide a rationale for the single conformer interpretation. The data are consistent either with a reaction in which N_2 and SO are expelled simultaneously or with the formation of a short-lived intermediate arising from N_2 loss which rapidly eliminates sulfur monoxide. Intermediate formation of thiatriazole *S*-oxide cannot, however, be ruled out unambiguously.

Since thioazides cyclize readily to thiatriazoles, whereas thioazide *S*-oxides are not observed to cyclize, MO calculations have been carried out for the ring closures **2**→**3** and **5**→**6** (R = H). Orbital correlation diagrams for each potential energy surface show that ring formation is "allowed" in both cases. It is suggested that the variable chemical behavior of thioazides and their *S*-oxides is due to disruption of aromatic character in the hypothetical thiatriazole *S*-oxide product.

We previously investigated the reaction between thiobenzoyl chloride *S*-oxide and the azide ion in an attempt to obtain the unknown 5-phenyl-1,2,3,4-thiatriazole *S*-oxide.[1] At −80° in ethanol a thermally unstable yellow precipitate is formed. The IR spectrum of the latter in methylene chloride at the same temperature indicates that substitution of chloride by azide has taken place, but that the resulting thiobenzoyl azide *S*-oxide has not cyclized to thiatriazole *S*-oxide. The presence of azide was inferred from the intense absorption at 2120 cm^{-1}. By contrast ordinary thiatriazoles exhibit no azide band in the IR and exist only as the ring closed compounds.[2] On heating of thiobenzoyl azide *S*-oxide to room temperature decomposition takes place with formation of nitrogen, sulfur dioxide, sulfur and benzonitrile according to Scheme 1.[1]

$$C_6H_5C(=SO)Cl + N_3^- \xrightarrow{-80°} C_6H_5C(=SO)N_3 \xrightarrow{\Delta} C_6H_5CN + N_2 + SO$$

$$SO \longrightarrow \tfrac{1}{2}S + \tfrac{1}{2}SO_2$$

Scheme 1.

The aim of the present paper is to investigate the kinetics and thermodynamics of the decomposition of thiobenzoyl azide *S*-oxide. In particular the question of possible intermediates in the step from azide to benzonitrile is considered. For example thiatriazole *S*-oxide or thiobenzoyl nitrene *S*-oxide species are conceivable although characteristic nitrene reactions were not observed in the previous investigation.[1] Furthermore the question of an open versus a closed structure for thioacyl azide *S*-oxides and thioacyl azides will be discussed from an MO viewpoint.[3]

RESULTS

Differential thermal analysis

For relatively rapid reactions in solution at low temperatures, Differential Thermal Analysis (DTA) was introduced as a promising analytic method,[4-6] since thermochemical as well as kinetic information may be obtained. In the present case tetrabutyl ammonium azide was combined with a solution of thiobenzoyl chloride *S*-oxide thermostatted at −80° to give **5** (R = C_6H_5–). No temperature difference signal could be detected, indicating the absence of a significant enthalpy for the spontaneous azide forming process. However when the mixture was heated a single peak with an initial temperature of ~−40° and a maximum temperature of ~−11° was observed. The reaction enthalpy of the corresponding process is calculated to be −45.6 ± 1.7 kcal mol^{-1}. Kinetic evaluation of the signals by direct application of the formula of Borchardt and Daniels,[6] leads to an activation energy of 20.2 ± 0.5 kcal mol^{-1} and a log A of 16.3 ± 0.5 ($\Delta S^*(-11°) = 6.3$ e.u.; standard errors, A in sec^{-1}; *cf.* Table 1) which approximately agrees with values from direct digital computer regression. (See Experimental section).

In order to specify the type of reaction, a determination of the shape index S' and the reaction type

Table 1. Kinetic and mechanistic data from DTA experiments under different conditions

Concentration of reactant mol dm^{-3}	Solvent	Reaction enthalpy kcal mol^{-1}	S_{exp}	M_{exp} 10^3 kcal/mol$^{-1}\cdot$K^{-1}	Activation energy kcal mol^{-1}	lg k_∞ (k_∞ in min^{-1})	Specific temperature difference û − m · u
0.020	ethanol	49.2	0.53	5.1	20.0	16.5	7.203
0.021	CH_2Cl_2	51.6	0.54	4.8	19.3	15.5	6.965
0.033	CH_2Cl_2	56.4	0.55	5.1	21.3	17.0	6.460
0.034	CH_2Cl_2	−55.2	0.59	4.7	19.0	15.1	7.195
0.036*	CH_2Cl_2	61.2	0.61	4.3	21.2	17.5	5.820
mean values			0.56 ± 0.03	4.8 ± 0.2	20.2 ± 0.5	16.3 ± 0.5	6.729 ± 0.264
theoretical values for first-order reaction			0.55	4.7			

Heating rate: 1.5 K min^{-1}.
*Heating rate 0.55 K min^{-1}.
S = +6.3 e.u. (−11°)

index M[8] is necessary. With a kinetic cell constant of $c = 0.17$ min^{-1}, a specific temperature difference[9] of û − 6.73 (Table 1) and maximum temperature differences of θ_m − 0.7–1.4 K, these mechanistic indices were taken directly from the curve and extrapolated to the ideal conditions of a non-isothermal rate curve, c = and θ_m − 0. The mean values from five experiments are, S = 0.56 ± 0.034 and M = 0.0048 ± 0.0002 while the theoretical values for any first-order reaction are S = 0.55 and M − 0.0047.[8,9] Excellent agreement with a rate-controlling first-order reaction is obtained.

Molecular orbital calculations

We have carried out potential energy surface calculations for the two ring closures **2**→**3** and **5**→**6** with the CNDO-B parameterization.[10] The problem has been reduced to manageability by considering explicitly only the parent systems (R = H).

Two isomeric structures have been found for each of the open species **2** and **5** by optimization of the geometry as a function of energy. Bond lengths and angles are given in Fig. 1. Likewise the structures of thiatriazole **1** (R = H) and the corresponding *S*-oxide were geometry-energy optimized. The calculation leads to an out-of-plane SO bond (58°). The potential energy surface for ring closure was mapped by a step-wise transformation of **2** and **5** to **3** and **6** respectively. For simplicity the thiatriazole reaction (**2**→**3**) was assumed to be planar throughout. In the case of the *S*-oxide, two closure pathways were explored. The first involved maintainance of all atoms in a common plane with the SO bond gradually assuming an out-of-plane position. The second closure began with the plane of the CSO atoms perpendicular to the N_3CS plane. The initial 90° disposition of the SO bond was progressively reduced to the *S*-oxide value of 58°. Orbital correlation diagrams for each ring-closure have been constructed. Figures 2 and 3 correspond to the in-plane closures. The orthogonal geometry *S*-oxide calculation produced a qualitatively similar diagram.

DISCUSSION

Treatment of thiobenzoyl chloride **1** with azide at temperatures as low as 100° leads to thiatriazole (R − C_6H_5) in excellent yield.[12] The ring-closure reaction clearly involves a low activation barrier since the thiocarbonyl azide **2** cannot be detected at 100° when the mixing of the reactants, thiobenzoyl chloride and tetra-

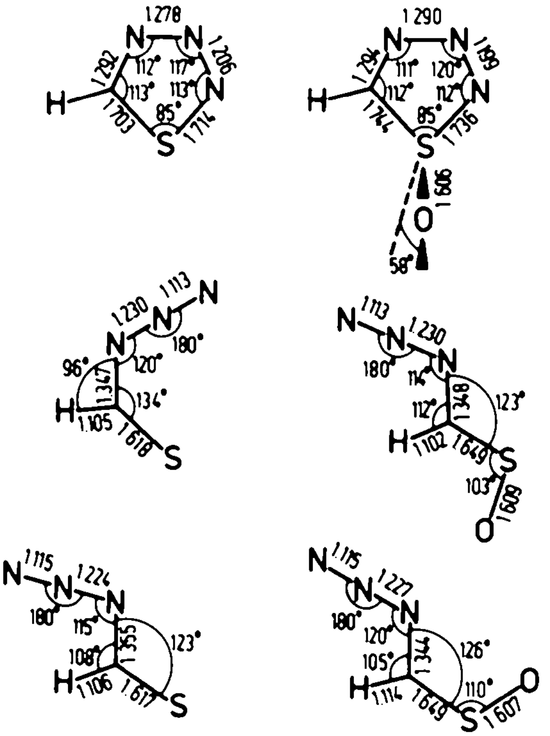


Fig. 1. CNDO/B[10] optimized geometries for 1,2,3,4-thiatriazole, planar thioformylazide conformers and the corresponding *S*-oxides. Only two of the four planar azide *S*-oxide conformations were considered explicitly (bond lengths, Å; bond angles, deg).

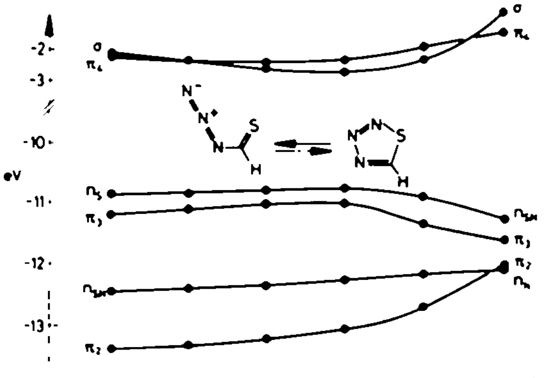
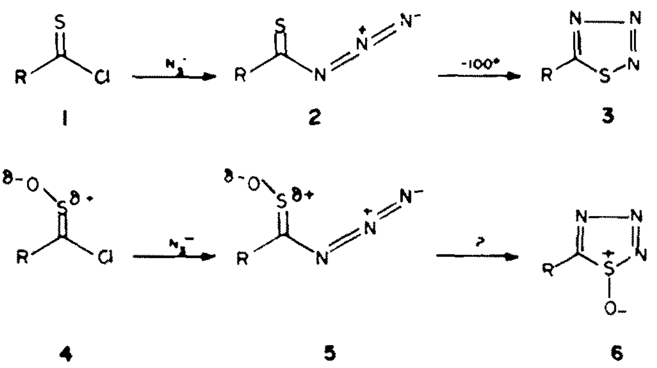


Fig. 2. Orbital correlation diagram for the planar cyclization of thioformylazide to thiatriazole (CNDO/B). Only the two lowest virtual orbitals and the four highest filled MOs are shown.



Scheme 2.

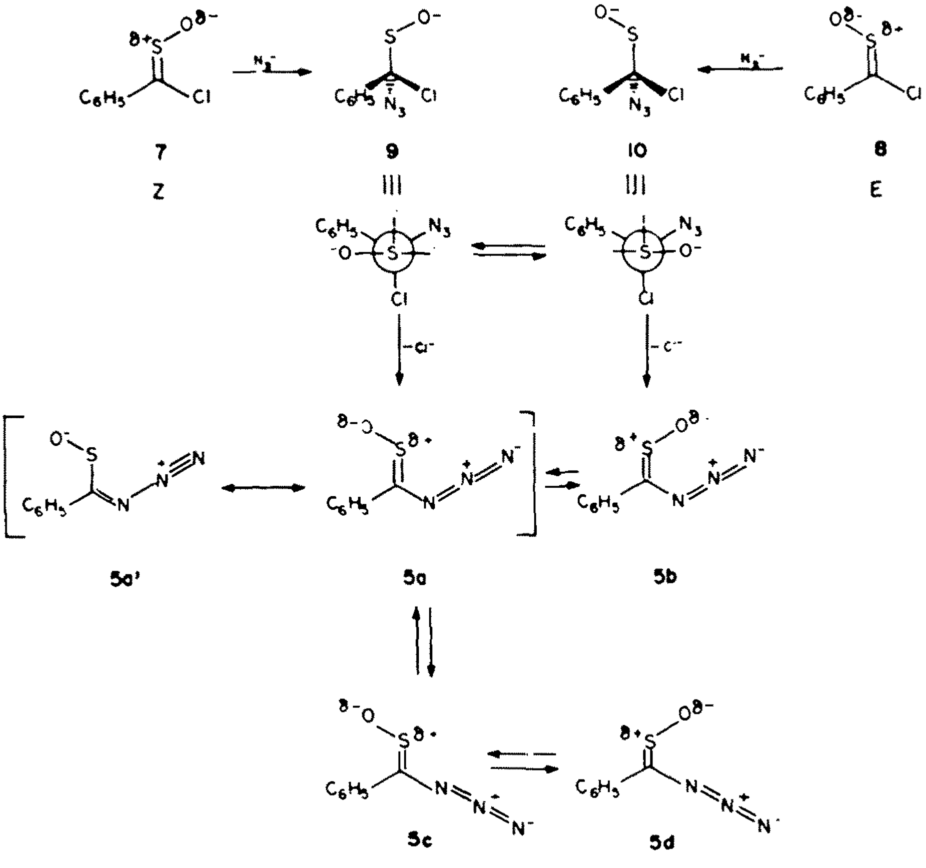
butylammonium azide, and the formation of the thiatriazole is monitored with UV spectroscopy.[13]

By contrast the analogous reaction sequence of the *S*-oxide (**4**→**6**), leads only to thiobenzoyl azide *S*-oxide **5** as confirmed by IR. Azide **5** fragments on heating without giving evidence for the intermediacy of the cyclic *S*-oxide **6**.[1]

Azide **5** can, in principle, exist in four distinct stereoisomeric forms, if non-planar conformers are ignored; i.e. **5a–d** (Scheme 3).

However there are two observations which require clarification. Both *Z* and *E* isomers of thiobenzoyl chloride *S*-oxide (i.e. **7** and **8**) lead to the same product composition when treated with ammonium azide.[1] Secondly the absence of a temperature difference signal apart from the main peak at −11° would seem to rule out both an azide isomerization with a significant enthalpy and the simultaneous decomposition of more than one azide conformer. The occurrence of two or more independent azide reactions can be expected to result in a clearcut dissection of the main peak in contrast to observation. For a common frequency factor, peak differentiation holds even if the various activation energies differ by only a few tenths of a kcal mol^{-1}.[12,13]

A reconciliation of the formation of azide intermediates from stereoisomeric starting materials and the apparent decomposition of only a single isomer is evident from Scheme 3. Substitution of the chloride *S*-oxides **7** and **8** requires the intermediacy of the tetrahedral species **9** and **10**. These may equilibrate by rotation around the C–S bond and thus lead to the same isomeric mixture of azides. Once formed the four sulfine



Scheme 3.

azides **5a–d** are capable of interconversion by rotation about the C–S and C–N bonds. In general thioketone *S*-oxides which do not bear electron donating substituents on carbon (e.g. **7** and **8**) can be isolated as non-interconvertible isomers at room temperature.[14] The energy barrier for isomerization amounts to 18–23 kcal mol^{-1}.[15] Electron donating substituents, however, can lower the barrier significantly as expressed by structure **5a′**. Accordingly the C–N and C–S CNDO–B bond orders for **5** (R = H) are 1.4 and 1.9 respectively. The calculated energy barriers for rotation around the same bonds are 5 and 18 kcal mol^{-1} respectively. This is to be compared with the corresponding values for the parent species, $CH_2\overset{\delta+}{S}-\overset{\delta-}{O}$: C–S (bond order) = 2.0, $\Delta E_{rotation}$ = 24 kcal mol^{-1}.[16]

Consequently we conclude that the various azide isomers are rapidly interconverting under the conditions of our experiments (≥ −80°) and that the corresponding equilibria have no detectable energetic influence on the subsequent decomposition reaction. Furthermore the DTA signal reveals no mechanistic evidence for a consecutive reaction. Thus the rate of decomposition of any intermediate must be considerably faster than its rate of formation. If formed the thiatriazole *S*-oxide **6** would therefore appear to be a relatively high energy species. In addition the moderately positive activation entropy of 6.3 eu (−11°) is suggestive of fragmentation rather than ring closure. Since, however, the latter measurement has been made on a solution, interpretation of $\Delta S^{\ddagger}$ must be made with caution.[17] Ring closure generally leads to moderately negative values, but examples of small positive activation entropies have been recorded.[18]

The reasons for the apparent lack of a thiatriazole *S*-oxide intermediate are not altogether obvious. Although thiophene *S*-oxides are highly reactive, dimerizing in a Diels–Alder fashion,[19] thiadiazole *S*-oxides are stable monomers.[20] Thus while **6** may be expected to be energy rich, its existence is not inconceivable. A possible explanation for the differences in behavior of **2** and **5** lies in the recognition that ring formation represents a type of electrocyclic reaction. It has recently been suggested theoretically that electrocyclization between termini bearing lone electron pairs can lead to unexpected patterns with regard to the "allowedness" or "forbiddeness" of the reaction.[21] The variable substitution at sulfur for **2** and **5** motivated a theoretical investigation of the ring closures for these systems in order to learn whether the two reactions might fall into different categories. Molecular orbital correlation diagrams for the two processes are given in Figs. 2 and 3. It is immediately evident that both thiocarbonyl azide and sulfine azide ring formation reactions are "allowed". All bonding molecular orbitals of the starting substrate correlate smoothly with bonding levels in the product.

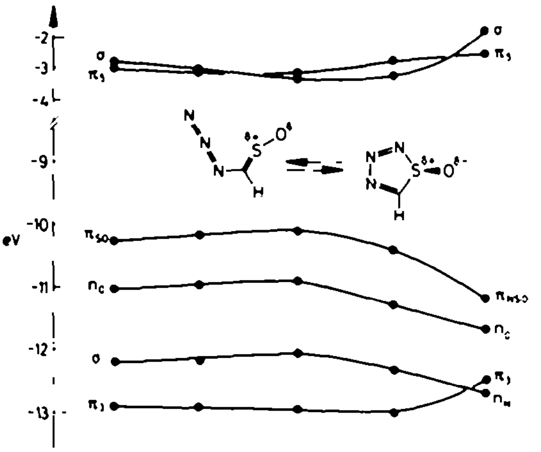
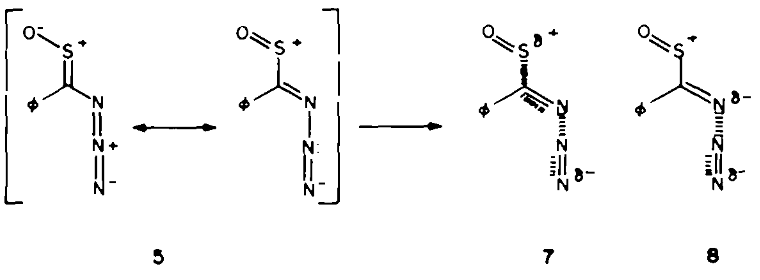


Fig. 3. Orbital correlation diagram for the planar cyclization of thioformylazide *S*-oxide to thiatriazole *S*-oxide (CNDO/B). Only the two lowest virtual orbitals and the four highest filled MOs are shown.

A plausible explanation for the variable ring closure behavior of **2** and **5** (R = C_6H_5) is found in the relative thermochemical stability of acycle and the corresponding ring. The thioazide closure is rapid and exothermic. Oxidation of the thioazide **2** to its *S*-oxide **5** is energy lowering both by the introduction of a new S–O bond and by an attendant gain in resonance energy due to conjugation of the extended π-system with S–O. Introduction of oxygen on the product side creates a new S–O bond, a stabilizing influence, but disrupts the aromatic character of the thiatriazole ring. The net effect relative to the thioazide/thiatriazole couple is that the *S*-oxide is stabilized on the acyclic side and destabilized on the ring side. The changes may be enough to convert an exothermic thioazide closure into an endothermic process for the oxidized species. Regardless of the quantitative features of the comparison, Hammond's postulate allows that a greater activation energy can therefore be expected for the formation of *S*-oxide **6**. The erection of a kinetic barrier by displacement of the equilibrium (**2** ⇄ **3**, **5** ⇄ **6**) in principle permits other decomposition pathways to become competitive. In particular the unimolecular fragmentation depicted by transition states **7** or **8** may be operating. Nitrogen and SO can be expelled simultaneously or a short-lived intermediate arising from N_2 loss could rapidly eliminate SO to give the observed products.

The slightly positive entropy for the decomposition of *S*-oxide **5** favors such a mechanism. In spite of these considerations, the formation of cycle **6** followed by rapid loss of N_2 and SO cannot be ruled out unambiguously.



Scheme 4.

EXPERIMENTAL

Equipment. A modified version of the solution DTA apparatus[22] developed in Mülheim/Ruhr[23] was employed. The instrument has Teflon stirring disks, copper/constantan thermocouples and 5 ml test tubes for sample and reference solutions installed in a alumina block. Temperature differences and absolute temperatures were observed by using a two-channel recorder (BD 6 of Comp. Kipp and Zonen, Delft, The Netherlands; measuring ranges 0.02–5 mV).

Procedure. A solution of thiobenzoyl chloride S-oxide[1a] and the pure solvent (ethanol or CH_2Cl_2, reference glass) were separately thermostattted at ~193 K and treated with a solution of tetrabutylammonium azide in the cold solvent (0.75 ml). Heating during the DTA was accomplished by temperature control of the block at a rate of 1.5 or 0.55 K min^{-1}.

Evaluation. Enthalpies were determined from the area between measured curves and base lines by means of the equation

$$\Delta H = \frac{c \cdot C_p}{n_0}\int_0^\infty \theta\,dt \qquad (1)$$

ΔH reaction enthalpy
c kinetic cell constant
C_p heat capacity
n_0 amount of reactant
t time (min)
θ temperature difference sample/reference.

The kinetic evaluation was based on the equation of Borchardt and Daniels;[4] hence, the rate constant for a first-order reaction is

$$k = \frac{c\theta + \frac{d\theta}{dt}}{c\int_t^\infty \theta\,dt - \theta}. \qquad (2)$$

For complex reactions this equation cannot be used. However, application to the S-oxide rendered straight lines in the Arrhenius diagram for points from the first part of the DTA curve (positive slope). Considering the temperature-dependence of c, for the S-oxide experiments we obtained straight lines for the points before the maximum. Changes of Cp, in general, were <1% in this range and were neglected. The formal activation energies of Table 1 may consequently be correlated to a first-order reaction.

The validity of a first-order reaction over the total temperature range was confirmed by an additional mechanistic analysis based on the curve half widths h and the shape indices S. For this evaluation both values have to be corrected to the ideal kinetic conditions appropriate for an infinitely high cell constant ($c \to \infty$) and a neglegible temperature difference ($\theta_m \to 0$). The ideal values are:[8]

$$h_\infty = \frac{h + \left(h - \frac{m}{c}\ln 2\right)(0.36 + 0.02\ln(uc))\frac{\theta_m}{u}}{1 + \frac{3.45}{(u+11)uc}} \qquad (3)$$

and

$$S_\infty = \frac{(uc)^{1.25+0.01\theta_m}}{[(uc)^{1.25} + 0.44][1 + (0.18 + 0.069uc)]\frac{\theta_m}{u}} \cdot S \qquad (4)$$

θ_m = maximum temperature difference
m = heating rate R = gas constant

the kinetic parameter u (dimension: time) is available from the activation data of the overall reaction by numerical regression.

If a cell constant of 0.17 and the u values presented in Table 1 are used, the corrected S values are 0.55 indicating a rate-controlling first-order reaction over the total range studied.[7,8] Independent proof is given by the determination of the reaction-type index[8] which is also available from the half width h_∞ and the parameter u:[8]

$$M = \frac{Rmu(\ln 10)^2}{h_\infty}. \qquad (5)$$

As Table 1 demonstrates, the M values as a function of solvent and heating rate reveal no considerable deviation from the quantity M = 0.0047 kcal mol^{-1} · K in accord with an undistorted first-order reaction.

Simulation of the DTA curves. The third experiment of Table 1 was monitored by generating the theoretical DTA curve by numerical regression using the HP-65[24] pocket calculator. The best-fitted data are:

E = 18.8 kcal mol^{-1}, $\log k_\infty$ = 15.7, c = 0.19 (u = 4.5 min)

(neglecting temperature-dependence of the thermopower).

As Fig. 4 shows, there is a satisfying correspondence of the computer curve with the experimental curve though the proposed activation energy and frequency factor slightly differ from those evaluated via eqn (2). One reason for this is that the simple computer program used is based on a fixed cell constant while the real cell constant increases from 0.14 to 0.22 during the run. However, since the influence of the cell constant on the curve shape is poor in the initial range, but strong in the final range, the curve can be approximated by taking a constant c which must be somewhat higher than the value at the curve maximum, c = 0.17.

Acknowledgements—We thank Mr. Lindner for his assistance in the measurements, and the Danish Natural Science Research Council for financial support.

REFERENCES

[1]A. Holm and L. Carlsen, *Tetrahedron Letters* 3203 (1973).
[2]A. Holm, *Adv. Heterocycl. Chem.* **20**, 145 (1976).
[3]Organo-Sulfur Mechanisms IV; For part III see J. P. Snyder, *J. Am. Chem. Soc.* **96**, 5005 (1974).
[4]R. C. Mackenzie, *Differential Thermal Analysis*, Vols. 1 and 2. Academic Press, London (1970/72).

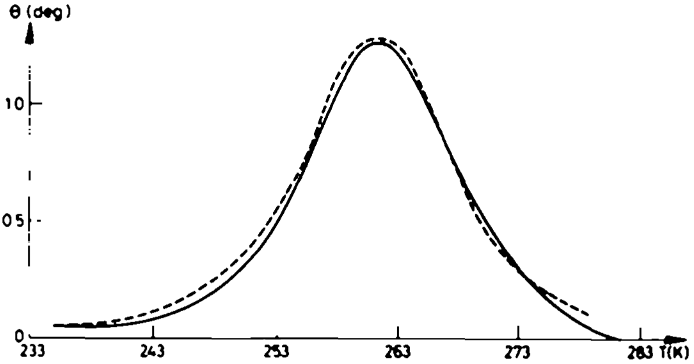


Fig. 4. DTA curve of the decomposition reaction of 0.032 M thiobenzoyl azide S-oxide in methylene chloride, ——— experimental (m = 1.5 K min^{-1}). – – – – – – computer simulation (m = 1.5 K min^{-1}), E = 18.8 kcal mol^{-1}, lg k = 15.7, c = constant = 0.19 min^{-1}.

[5] E. Koch, *Angew. Chem.* **82**, 306 (1970); *Angew. Chem. Int. Ed. Engl.* **9**, 288 (1970).

[6] H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.* **79**, 41 (1957).

[7] H. E. Kissinger, *Anal. Chem.* **29**, 1702 (1957).

[8] E. Koch, *Angew. Chem.* **85**, 381 (1973); *Angew. Chem. Int. Ed. Engl.* **12**, 381 (1973).

[9] E. Koch and B. Stilkerieg, *Thermochim. Acta* **17**, 1 (1976).

[10] R. J. Boyd and M. A. Whitehead, *J. Chem. Soc. Dalton Trans.* 73, 78, 81 (1972).

[11] A. Holm and L. Carlsen, in preparation.

[12] E. Koch, *Chem.-Ing.-Tech.* **44**, 111 (1972).

[13] K. Heide, G. Kluge, W. Reiprich and H. Hober, *Therm. Anal. Proc. Int. Conf.* (*4th*) **1**, 123 (1975).

[14a] J. F. King and T. Durst, *J. Am. Chem. Soc.* **85**, 2676 (1963); *Idem. Can. J. Chem.* **44**, 819 (1966); R. B. Bates and G. A. Wolfe, *J. Am. Chem. Soc.* **90**, 6854 (1968); B. Zwanenburg, L. Thijs, J. B. Broens and J. Strating, *Recl. Trav. Chim. Pays-Bas* **91**, 443 (1972); A. Tangerman and B. Zwanenburg, *J. Chem. Soc. Perkin Trans. II* 1141 (1974); [b]*Idem. J. Chem. Soc. Perkin Trans. II* 352, 916 (1975).

[15] B. F. Bonini, L. Lunazzi, G. Maccagnani and G. Mazzanti, *J. Chem. Soc. Perkin Trans. I.* 2314 (1973).

[16] J. P. Snyder and D. N. Harpp, *J. Chem. Soc. Chem. Commun.* 1305 (1972).

[17] W. P. Jencks, *Catalysis in Chemistry and Enzymology*, pp. 605–614. McGraw-Hill, New York (1969).

[18] M. R. Willcott, R. L. Cargill and A. B. Sears, *Progress in Physical Organic Chemistry* (Edited by A. Streitweiser, Jr. and R. W. Taft), Vol. 9, p. 25. Wiley-Interscience, New York (1972).

[19] J. L. Melles and H. J. Backer, *Recl. Trav. Chim. Pays-Bas* **72**, 491 (1953); W. Davies and F. C. James, *J. Chem. Soc.* 15 (1954); W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.* **76**, 1932 (1954); cf. C. D. Hurd, *Quart. Rep. Sulfur Chem.* **4**(A), 90 (1969).

[20] H. Meier, G. Trickes and H. P. Braun, *Tetrahedron Letters* 171 (1976); and refs therein.

[21] B. Schilling and J. P. Snyder, *J. Am. Chem. Soc.* **97**, 4422 (1975).

[22] E. Koch, *Anal. Chem.* **45**, 2120 (1974).

[23] E. Koch, *Chem.-Ing.-Tech.* **37**, 1004 (1965).

[24] For such studies, programs 50397A and 50718A of the "HP-65 User's Library", Hewlett Packard Comp. Europe, Meyrin-Geneve, Switzerland, were developed.