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APPLICATION OF THERMAL ANALYSIS TO ORGANIC CHEMISTRY: A REVIEW

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ABSTRACT

This review covers some of the important contributions of thermal analysis in organic chemistry research since the VIIth International Congress on Thermal analysis in 1985, up to the present IXth Congress in 1988. During this period the trend of sophisticated use of thermal analysis for the study of fundamental aspects of chemistry became increasingly notable.

INTRODUCTION

This review includes the investigation of organic reaction, thermal stability of pharmaceuticals and explosives as well as kinetics of decomposition of organic materials. Thermal analysis was used to explore the correlation between specific heats and the effects of acoustic and optic modes. The investigation of phase diagrams, phase transformation were continued and expanded.

Thermal analyses are non-specific, not identifying particular chemical species. Combining thermal analysis with X-ray and IR analyses is a common practice. Evolved gas analysis (EGA) was added for obtaining information. New technologies of low temperature and extremely high pressures may help to elucidate properties and behavior of organic substances, on heating. A special aspect is the coupling of thermal analysis with impressive novel methods: positron lifetime measurements and NMR relaxation studies, employed in the research of triglycerides to clarify mechanisms of phase transitions.

A. Thermal investigation of organic reactions

Kinetic measurements of an organic reaction may be carried out by numerous well-known analytical procedures. It is an interesting approach to look for a correlation between the thermal analysis of reaction products and the reaction parameters which lead to their formation. A study was carried out investigating the oxidation of phenol derivatives by iodine (1). The TGA

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data show that fragmentation of the obtained polymeric redox products of aminophenols starts at low temperatures (66-190°C) where loss of N_2 and NH_3 occurs. The instability of the amino dimers/polymers may be attributed to weak bonds containing nitrogen between the rings. This would indicate high values of the rate constants. Conversely, fragmentation of the redox products of bromophenols starts at higher temperature (>210°C). This may be attributed to the stabilization of the ring system due to the electronegativity of bromine.

The structure of separated pure, products obtained by oxidation of bromo- and chlorophenols with iodine were investigated by DTA and TGA and correlated with IR and microanalysis to elucidate their molecular formulae (2). The decomposition of the halogenated phenols shows mass loss due to the evolution of crystallization water and functional decomposition of the halogenated phenols. The nature of the functional groups existing in the redox products - bromo- and chloro-phenols - was identified by IR. These data support the results of DTA analysis which indicate the decomposition of the phenol derivative, i.e. sublimation of iodine molecules in addition to the loss of crystallization water. Though aromatic mono-amines form salt-type derivatives with acids through the lone electron pair on the nitrogen atom similarly to aliphatic amines, the different proton affinity of these amines may lead to different thermal behaviour of the two classes of amino salts.

The thermal dissociation of hydrochlorides of aromatic mono-amines was investigated by TG, DTG and DTA (3). The dissociation of the majority of these derivatives proceeds in one step up to 88%, followed by a slow step. This thermal behaviour is also typical of hydrochlorides of other organic nitrogen bases. Some of the aromatic monoamino salts of hydrochloric acid studied, decompose in two distinct stages. The first corresponds to the release of HCl whereas the second one is the volatilization of the free amine. The latter thermal decomposition pattern is characteristic of compounds exhibiting the complex structure of an aminium cation.

The study of substances from which qualitatively different products originate on heating may prove to be an important field in the thermal studies. In a DSC study of cyclocondensation of six derivatives of 1,3 dimethyl-4-alkylamine-5-nitrosouracils yielding the 8-substituted theophyllines (4), it was revealed that the course of the reaction can be affected by several parameters. Due to the strongly exothermic character of the reaction, different behaviour is observed under isothermal and non-isothermal conditions. For instance self heating of the sample may result in the formation of temperature gradients. It appears that the use of the non-isothermal method is not suitable for complex mechanisms, especially if one is interested in autocatalytic processes.

B. Thermal stability and kinetics of decomposition

The thermal decomposition curves can be analyzed according to kinetic models to yield the best fit to a specific reaction mechanism in addition to the data of the reaction enthalpy.

This class of studies includes the thermal decomposition of 3(4,5-Dimethyl-2-thiazolyazo)-2,6 diamino pyridine which constitutes a novel ligand of Co (III). Three methods employed for mathematical analysis showed that the best α-functions were those for nucleation-growth mechanism indicating the formation of radicals and dinitrogen. The observed enthalpy change, which is considerably lower than the carbon-nitrogen bond energy, can be explained by the partial formation of dinitrogen and *trans* isomer (5).

Tanaka (6), through the kinetic study of the thermal decomposition of cytidine and uridine was able to compare his own kinetic model with that of Friedman (7). The decomposition which was studied by TG and DTA, began near the first and terminated at the second endotherm. The results were plotted against reciprocal absolute temperature at three heating rates. The mathematical models of Friedman (7) and Tanaka (6) were applied. Despite the differences of approach, very close values of the activation energy for both cytidine and uridine were obtained by the two methods.

A generalized formalism of the selection of the most probable mechanism function and computation of activation energy, the pre-exponential constant and reaction order has been recently proposed by Rangzu (8), for the exothermic decomposition reaction of energetic material. The main advantage of this approach is that all the parameters can be obtained by a single non-isothermal DSC curve. Constructional details of the Shanghai Balance Manufacturers' CDR-1 DSC instrument were given.

Thermal stability of functionally similar molecules differing either in their cyclic or acyclic structure was examined for a tetramethylenetetranitramine pair (9). The linear molecule is a chemical propellant. High rate thermolysis (dT/dt = 1K sec-1) liberates, with a few exceptions, the same products for both molecules. Competitive N-N and C-N bonds fission occurs as predicted by the IR data and molecular structure. An evaluation of the relative stability of the cyclic and acyclic molecules was obtained by comparing the IR spectra of the slowly heated thin film of the sample. The linear molecule melts at 490°K and starts decomposing at 500°K, whereas the cyclic one begins to decompose in the solid phase below its liquefaction temperature of about 550°K. Thus the linear molecule appears to be less thermally stable than the cyclic one. On the other hand, once the decomposition temperature is reached the decomposition rate of the cyclic molecule is faster than that of a linear one.

The thermal stability of proteins is equivalent to thermal denaturation. Previous studies reported stability data at a single pH-value. The stability of various proteins was examined in widely different buffer solutions, making a comparison of their thermal stabilities impractical. Paulson (10) studied the stability of bovine whey proteins: β-lactoglobulin (β-lg), α-lactalbumin (α-la) and serum albumin (BSA). β-lg was shown to be the most thermostable. At acidic pH values BSA was the least thermostable. At alkaline pH values, however, α-la had lower thermal stability than BSA. When mixed the proteins seemed to denaturate independently of each other.

Another study on 22 amino acids, the most significant constituents of proteins, has been reported recently (11). The aim of the study was to correlate the thermal behavior of the acids with their structural groups. It was confirmed that in the α-amino molecule, the side chain which is responsible for specific characteristics of each amino acid, influences the thermal effects that occur during their heating. The high melting points may be attributed to the substantial electrostatic attraction between the oppositely charged groups in the crystal lattice. The apolar nature of the side chain in Alanine, Valine, Leucine, and Isoleucine results in sublimation effect previous to melting whereas the polar Asparagine, Glutamine, Arginine, Lysine, Ornitine, Glycine and Serine do not sublimate. Other features are discussed in detail.

Riboflavin is a water soluble vitamin (B_2). The only information on the thermal stability of riboflavin was that it melted and decomposed simultaneously at a temperature of about 290°C. A study was undertaken to carry out a detailed thermal investigation of this compound in order to be able to study the thermal decomposition of riboflavin complexes with metal ions. This was needed to obtain useful data on the metal-ligand bonds (12). It was revealed that riboflavin with its high thermal stability, decomposes through four rapid stages.

The elimination of N_2 from 2H-tetrazoles can be initiated by photochemical or thermal activation in dilute solutions as well as in PAMMA matrices e.g. as used in photo-resist systems. The thermal behaviour of pure diaryl-substituted 2H-tetrazoles was investigated in dilute solutions (13). The mass losses found for the first step exceeded the values calculated for N_2 only. The excess losses are caused by the evaporation of volatile compounds formed during stabilization of the reactive diphenylnitrileimines.

Melamine is known to undergo condensation on heating with elimination of ammonia and formation of insoluble products. Thermogravimetry and I.R. characterization show that two products of successive condensation can be reproducibly obtained (14).

A very special case of thermal decomposition having technological and economic importance is the pyrolysis of oil shale. The principles of non-isothermal kinetic analysis of the decomposition process are, in the eyes of Hoare and Stuart (15) "bedevilled by mathematical and computational problems." One may agree with this statement; most of the studies on thermal decomposition cited in this review deal with the selection of the most suitable kinetic model from an array of fairly complex ones. The authors (15) adapted numerical methods for the direct solution of non-isothermal kinetic equations and their use was illustrated by their application to the thermogravimetry of oil shale pyrolysis. Experimental TG-DTG profiles were obtained for kerogen concentrates of two Australian oil shales. No single kinetic model could be fitted to the experimental data, but functions based on multistage models provided good agreement between calculated and experimental TG-DTG profiles.

The TGA/DSC application to *in situ* combustion processes may be augmented in the future. The type of information obtainable from TGA and DSC curves of crude oil combustion is (a) the major crude oil transitions (b) the effect of clay (c) the effect of the sand grain specific area, (d) kinetic data and (e) combustion feasibility (16).

It is interesting to note that the DSC curves reveal less energy release than the true reaction heats of the oxidation of organic materials. This fact may be due to the low oxidation rate of some primary volatile products, especially CO, inevitably formed during the oxidation of organic and carbonaceous materials at the temperatures of DSC experiments. The measured heat is strongly affected by the experimental conditions and can be brought closer to the net heat of combustion by catalytic oxidation of the CO formed inside the measuring cell (17).

The interpretation of isothermal operation of DSC does not necessitate complex mathematical calculations. It was used to advantage by Torres-Gomez (18) for the measurement of enthalpies of sublimation. The investigated materials were naphthalene, benzoic acid and phenanthrene. The experimental set-up included DSC coupled to a vacuum system. The precision was found to be dependent on the rate of sublimation. The results compare satisfactorily with results obtained by torsion-effusion and calorimetry.

Studies of thermal behaviour of pharmeceutical compounds started more than a decade ago. With increasing requirements of purity, new original ways of thermal analysis applications are being worked out. Lovastatin is a. potent inhibitor of the rate-controlling enzyme in cholesterol synthesis. When Lovastatin is oxidatively stressed and subsequently melted in inert atmosphere and cooled, it yields a vitreous solid which exhibits a characteristic glass transition. The temperature range over which the glass transition occurs moves increasingly higher with increase of the extent of prior oxidation. The sample temperature Tg_2, at the midpoint of the transition, is sensitive to the extent of the oxidation of the particular sample. Thus a basis of a simple procedure for assessing the relative reactivity and purity of Lovastatin samples was established (19).

Nitrofurans constitute a fairly broad spectrum antimicrobial agent. The temperature at which the exothermic process of decomposition of a specific compound occurs may serve to establish the technological characteristics and criteria in the production of this compound as a pharmaceutical preparation or drug i.e. in drying and tabletting (20).

C. Specific heat and harmonic models

At the Bratislava (ICTA 85) Congress, Martin (21) presented the formalism allowing a direct analysis of the temperature dependence of the specific heat, which is a quantity rendered by experiment. This formalism permits determination of some of the crystal normal mode frequencies and their temperature dependence. Martin applied this approach to the analysis of the temperature dependence of the specific heat in 1,1,1-trichloroethane in the low temperature phase below 225°K (22). The contributions to the acoustic and optic modes were approximated. A value for the Debye temperature $(26.9 \pm 2.6)\mathrm{cm}^{-1}$ was deduced. The analysis of Cp vs T showed the probablility that lattice vacancies were present.

The temperature dependence of the specific heat in the α-phase of para-dichloro benzene allowed the determination of the Debye temperature and rotary lattice mode γ_3 both of which were previously undetermined for this compound (23).

D. Polymorphic transitions

Polymorphism is the capacity of a substance to exist in several solid forms which are chemically identical but have different physical properties such as melting points, X-ray diffraction patterns, dissolution rates, densities, thermal stabilities, optical characteristics, etc. Phase transition implies change in crystal structure and is accompanied by enthalpy changes which are considerably lower than those of melting or sublimation. The enthalpy changes are easily recorded by DSC, but this non-specific technique can only establish the existence of the transition at a particular temperature. In order to elucidate the exact nature of this transition, coupling with structure determining methods is necessary.

In the study of Reffner and Ferrilo (24) a combination of techniques: DSC, thermomicrophotometry, FTIR and thermomicroscopy were used to establish the existence of polymorphs and characterize their transformations. An example of application of these combinations of techniques is p-hexadecylaminobenzoic acid (HABA), which can appear in three polymorphic forms and as a liquid crystal. The combined techniques enabled the construction of energy level diagram of HABA transitions: form 1 can be obtained only from solution crystallization and transforms to form III. From melt LC are obtained which may transform, through reversible transition to form III. The II→III transition can be detected only by careful polarized light microscopic examination, while there is no change in the crystal shape and texture. This transition could not have been detected without the information gained by DSC (24).

The cohesive energy per molecule affects the rate of polymorphic transformation. In a study of the crystalline modifications of vinyl esters of long chain fatty acids (25) it was found that for vinyl myristate (VC_{14}) and laurate (VC_{12}) the β_1 form transforms to the β'_2 form faster than in the case of vinyl palmitate (VC_{16}).

The tightness of packing is another factor which strongly affects the possibility of phase transition. The phase behaviour of phospholipids with iso-branched and ω-cyclohexyl fatty acids was studied by DSC (25). A complicated phase behaviour with several gel-gel transitions was discovered with pronounced odd-even effect. The odd numbered compounds display much tighter packing in the gel phase than the even-numbered analogues.

The measurement of the differential enthalpies of long chain ionic surfactants can lead to a good approximation of the partial enthalpy content of the surfactant in the monomer and micellar state relative to the crystalline state (26). The large positive partial molar heat capacities of the monomeric surfactants are characteristic for hydrophobic solutes and the large heat capacity change for micelle formation arises from the loss of hydrophobic hydration in the process of micelles formation.

Several cyclic alkanes melt in two steps. The premelting transition reflects a cooperative loss of part of the crystalline order. The crystalline order is comprised of the contributions of the molecules conformation, orientation and position. The occurrence of any disorder results in an increase of entropy which can be broken up correspondingly into three terms. Drotlop and Moller (27) reported data on a series of cycloalkanes C_2H_{2n} with n = 12, 13, 14, 15, 16, 24, 36, 48, 72, 96 and discussed the entropies of transitions per methylene group.

The transition behaviors of small, medium and large size cycloalkanes are different allowing classification in three classes. For each class the contributions to the orientational and conformational disorders have different respective importance in the overall enthalpy of the transition.

Hiterto unreported solid-to-solid transitions for four alkylureas have been detected (28). Enthalpies and temperatures of fusion were determined within a wide program of measuring the enthalpies of sublimation of urea and its derivatives.

The fast thermal decomposition of energetic materials which serve as propellants and explosives may be different for different polymorphs and thus constitute a potential hazard in preparation, as some polymorphs are more shock sensitive than others. A disordered high temperature phase of a cyclic nitramine, previously discovered by IR spectroscopy was confirmed by DTA to be a plastic phase (29).

Solid to plastic crystal transitions were also analyzed in penta-glyceride neopentyl-glycol mixtures (30). Molecules of this type, which are highly symmetrical, show rotational transitions in the solid state. These transitions give rise to a new phase, the plastic crystal phase, between the anisotropic crystal and isotropic liquid phases. Some organic substances with plastic crystalline phases were investigated at high pressures up to 1750 bar (31).

In the ICTA Young Scientist Award Paper of 1988 the author showed the wide extent of information that can be obtained by thermal analysis for the kinetics of phase transformation in triglycerides (32). The transitions are affected by their respective chemical structures as well as by various experimental parameters. The series of triglycerides with acids of chain lengths ranging from 12 to 18 carbons show differing ratios of fusion enthalpy of the α-form (ΔH_α) and the β-form (ΔH_β). These differences lead to assumptions concerning the diverse mechanisms of polymorphic transitions in the otherwise very similar isomorphous substances. The very small value of $\Delta H_\alpha/\Delta H_\beta$ in trilaurin indicates that the $\alpha \rightarrow \beta$ transition occurs mainly in the solid state whereas the high value of this ratio in tristearin indicates that most of the α-form melts before transition and β-form nucleates and grows from the melt. These assumptions are strengthened by a whole array of experimental evidence, most important of which being the use of emulsifiers having chemical affinity to the triglycerides and varying degrees of structural compatibility. Especially interesting is the possibility of detecting the conditions for the stabilization of the intermediate β', which cannot be detected in pure triglycerides. DSC thermograms of mixtures of triglycerides with different chain lengths, a composition close to that of natural fats show three endotherms which can be identified as the fusion enthalpies of α, β' and β respectively. This effect may be affected by thermodynamic factors due to the stabilization of the orthorhombic packing when triglycerides with different chain lengths are mixed. The stabliization of thermodynamically unstable polymorphic forms in fats is of high technological importance in the food industry.

E. New techniques

Application of DTA under high pressure gas atmospheres were critically reviewed by Sawada et al. (33). Materials which are used under normal pressures are often characterized more clearly by analysis under high-pressure gas atmospheres e.g. separation of superimposed DTA peaks, evaluation of oxidation stability, determination of self-ignition temperatures etc.

A low-temperature DTA apparatus was constructed for studies below 80K using liquid hydrogen as coolant (34). The performance of the apparatus was examined by a test run for crystalline ND_4HgCl_3. A glass transition was discovered for liquid 3-methyl-1-butene at 64.7K. Particularly valuable information was obtained with this apparatus for crystalline THF 16.9 H_2O doped with KOH. The phase transition at ≈62K may be ascribed to the ordering of hydrogen atoms. If this is the case, this observation may lead to more extensive studies of gas hydrates and the structural properties of the ordered phase will be raised to the stage of experimental research.

A new theory of sensing units in DTA instruments was presented by Shishkin (35) under the title "An introduction to time-space calorimetry" (35). The sensing units, volume-isothermal and surface-isothermal with a gas-phase thermal barrier were described. Construction principles of a single-run heat conduction type DSC, which can record heat capacity directly were discussed by Wunderlich (36).

A method for calorimetric determination of purity was described (37) using direct comparison between the measured melting curve with a simple R-C model of a heat flux model. The method is not restricted to eutectic systems or low impurity concentrations.

The combination of knowledge of the mass and energy changes occurring in a material, together with full information on the gas phase products as the temperature is scanned, gives a "new" insight into the system (38). For instance, the combination of TA-MS was used to study guar gum which is a series of closely related polysaccharides. The use of evolved gas analysis (EGA) may overcome the limitations of TA, due to the non-specificity of the thermal methods.

F. Special studies

DTA determination in combination with non-isothermal UV measurements was used for the study of the oxidation of malonic, tartronic, glyoxylic and monobromomalonic acid by the catalytic effect of ceric sulphate in dilute sulphuric acid (39). Novel one-step strategies were used for the determination of quantities typical of mechanisms.

Experimental data on thermal kinetics of organic peroxy esters were gained by using low pressure autoclave, DTA and isothermal storage tests (40).

Clay-stearic acid associations depend on the rate of escape of the acid, which is determined by the strength of bonding to the clay and the degree of dissociation of the acid on clay surfaces. The adsorption of fatty acids by clays is of interest, because of the possible catalytic effect of these minerals on the conversion of fatty acids to petroleum hydrocarbons. The exothermic peaks in DTA curves were attributed to the oxidation of stearic acid; the presence of the clay evidently has a catalytic effect on oxidation (41).

The loading of organics on activated carbon may impair the effectivity of the carbon to its application in the mining industry for the recovery of precious metals or in the treatment of waste water. A mass balance and TGA data were used to calculate the load of organics (42). During carbonization graphitizable aromatic organic compounds such as naphthalene and anthracene, phenanthrene and chrysene pass through a liquid or plastic-state mesophase, before hardening to a semi coke (43).

The effect of exposure of chloroquine and its salt derivatives to the sun was studied appropriately enough in Nigeria (44). The endothermic peak of melting was found to be suitable for the quantitative determination of chloroquine picrate in sun exposed samples.

The existence of polymorphic forms in triglycerides, the dependence of heats of fusion on chain lengths of the fatty acids and the kinetics of transformations were reported in a series of thermal studies (32, 45, 46, 47). The mechanisms of transformations were made clearer through the use of selected emulsifiers. All of them had chemical affinity to the triglycerides. However, only the emulsifiers which have, in addition to chemical affinity a degree of structural compatibility, are able to effectively retard polymorphic transitions (48). The credibility of the proposed mechanism was enhanced by NMR relaxation studies (49).

A further modern sophisticated method was coupled with differential scanning calorimetry to study the physical aging of tristearin: the positron lifetime measurements carried out in the department of Physics and Astronomy in Tuscaloosa (50).

REFERENCES

1. M.A. Zayed and F.A. Nour El-Dien, Thermochim. Acta, 128 (1988), 105.
2. M.A. Zayed and F.A. Nour El-Dien, Thermochim. Acta, 113 (1987), 117.
3. J. Lubkowski and J. Blazejowsky, Thermochim. Acta, 121 (1987), 413.
4. T. Gondova, P. Kralik and R. Domansky, J. Thermal Analysis, 32 (1987), 237.
5. B. Gallo, A.R. Arnaiz and C. Santiago, Thermochim. Acta, 124 (1988), 35.
6. Y. Tanaka, N. Takeda and D. Fujita, Thermochim. Acta, 115 (1987), 281.
7. H.L. Friedman, J. Polym. Sci. Part C., 6 (1964), 183.
8. H. Rongzu, Y. Zhengquan and L. Yanjun, Thermochim. Acta, 123 (1988), 135.
9. Y. Oyumi, T.B. Brill and A.L. Rheingold, Thermochim. Acta, 114 (1987), 209.
10. M. Paulsson, P.O. Hegg and H.B. Castberg, Thermochim. Acta 95, (1985), 435.
11. M.L. Rodriguez-Mendez, F.J. Frey, J. Martin-Gil and F.J. Martin-Gil, Thermochim. Acta, 134 (1988), 73.
12. J. Maslawska and M. Malicka, J. Therm. Analysis, 34 (1988), 3.
13. M. Feist, Ch. Csongar and L. Adler, J. Therm. Analysis, 32 (1987), 1957.
14. L. Costa and G. Camino, J. Thermal Analysis, 34 (1988), 423.
15. I.C. Hoare and W.I. Stuart, Thermochim. Acta, 113 (1987), 53.
16. S. Vossough, Thermochim. Acta, 106 (1986), 63.
17. G. Varhegyi, P. Szabo and F. Till, Thermochim. Acta, 106 (1986), 191.
18. L.A. Torres-Gomez, G. Barreiro-Rodriguez and A. Galarza-Mondragon, Thermochim. Acta, 124 (1988), 229.
19. J.F. Elder, Thermochim. Acta, 134 (1988), 41, (ICTA 88).
20. B.C. Stojceva-Radovanovic and B. Lj. Milic, Thermochim. Acta, 32 (1987), 485.
21. C.A. Martin, Thermochim. Acta, 92 (1985), 273.
22. C.A. Martin and G.A. Monti, Thermochim. Acta, 134 (1988), 27, (ICTA 88).
23. C.A. Martin and G.A. Monti, Thermochim. Acta, 134 (1988), 35, (ICTA 88).
24. J.A. Reffner and R.G. Ferrillo, J. Thermal Analysis, 34 (1988), 19.

25. Y. Shibasaki and K. Fukuda, Thermochim. Acta, 88 (1985), 211.

26. S. Bergström and G. Olofsson, Thermochim. Acta, 109 (1986), 155.

27. H. Drotloff and M. Moller, Thermochim. Acta, 112 (1987), 57.

28. G. Della Gatta and D. Ferro, Thermochim. Acta, 122 (1987), 143.

29. Y. Oyumi and T.B. Brill, Thermochim. Acta, 116 (1987), 125.

30. J. Font, J. Muntasell, J. Navaro and J. Li. Tamarit, Thermochim. Acta, 118 (1987), 287.

31. U. Wenzel and G.M. Schneider, Thermochim. Acta, 109 (1986), 111.

32. J. Schlichter Aronhime, Thermochim. Acta, 134 (1988), 1 (ICTA 88).

33. Y. Sawada, H. Henmi, N. Mizutani and M. Kato, Thermochim. Acta, 121 (1987), 21.

34. M. Oguni, N. Okamoto, O. Yamamuro, T. Matsuo and H. Suga, Thermochim. Acta, 121 (1987), 323.

35. Yu. L. Shishkin, J. Therm. Analysis, 32 (1987), 17.

36. B. Wunderlich, J. Therm. Analysis, 32 (1987), 1949.

37. S. Sarge, S. Bauerecker and H.K. Cammenga, Thermochim. Acta, 129 (1988), 309.

38. P.A. Barnes, Thermochim. Acta, 114 (1987), 1.

39. E. Koch, Thermochim. Acta, 101 (1986), 245.

40. A.C. Hordijk and J.J. De Groot, Thermochim. Acta, 101 (1986), 45.

41. L. Heller-Kallai, S. Yariv and J. Friedman, J. Therm. Analysis, 31 (1986), 95.

42. B.S. Camby and J.S.J. Van Deventer, Thermochim. Acta, 113 (1987), 341.

43. T. Hossam and J. Dollimore, Thermochim. Acta, 108 (1986), 211.

44. J.O. Edafiogho, J.R. Mulokazi, A.M. Mulokazi and S. Diete-Spiff, J. Therm. Analysis, 34 (1988), 115.

45. J. Schlichter, N. Garti and S. Sarig, JAOCS, 64 (1987), 529.

46. J. Schlichter, N. Garti and S. Sarig, Tenside Surf. And Deterg., 24 (1987), 1.

47. J.S. Aronhime, N. Garti and S. Sarig, JAOCS, 65 (1988), 1140.

48. J. Schlichter-Aronhime, S. Sarig and N. Garti, JAOCS, 65 (1988), 1144.

49. R. Azoury, J.S. Aronhime, S. Sarig, S. Abrashkin, J. Mayer and N. Garti, JAOCS, 65 (1988), 964.

50. W.W. Walker, JAOCS, 64 (1987), 754.