Thermochimica Acta, 73 (1984) 47–66
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL ANALYSIS OF UREA, FATTY ACIDS, AND THEIR ADDUCTS

FATMA I. KHATTAB, NARIMAN A. AL-RAGEHY and ABDEL KADER S. AHMAD

Analytical Chemistry Department, Faculty of Pharmacy, Cairo University, Kasrel Aini, Cairo (Egypt)

(Received 12 July 1983)

ABSTRACT

The thermal analysis of urea and its decomposition product, biuret, was achieved. The calorimetric method was found to be suitable for the determination of the purity of urea. Some selected fatty acids varying in chain length and saturation (butyric, caproic, lauric, myristic, palmitic, stearic and oleic acid) were also examined. Attempts at their characterization and identification were successful. Determination of their boiling or melting points was possible by thermal analysis.

The possibility of adduct formation between urea and fatty acid was also studied using either the dissolved urea technique or simply by physical mixing. The stability of the formed adducts, mechanism of dissociation, their dissociation temperatures and heat of reaction (ΔH) were also investigated.

The boiling point, melting point, ΔH values and decomposition temperatures for each series studied were found to increase with chain length and decrease with unsaturation.

Various thermal analysis techniques were used, namely, diferential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG) and derivative thermogravimetry (DTG).

INTRODUCTION

Research on urea adducts by thermal analysis has dealt mainly with *n*-paraffins [1–7] and some polyesters [8]. In this work, a thorough study of the thermal behaviour of urea, using various thermal analysis techniques, was achieved. Similarly, different fatty acids were examined in an attempt at their characterization and differentiation. Adduct formation between these fatty acids and urea under various conditions was studied. Correlations between the thermal behaviour of different adducts and their constituents were also considered. The possibility of the determination of purity and some physical constants (melting point, boiling point, decomposition temperature and heat of reaction) using thermal analysis was also investigated.

EXPERIMENTAL

Materials

(1) Urea (A.R.) May and Baker;

(2) biuret, prepared by heating urea for 1–2 min just above its melting point [9];

(3) fatty acids, butyric acid (B.D.H), caproic acid (B.D.H.), lauric acid (Schering Kahlbaum A.B., Berlin), myristic acid (B.D.H.), palmitic acid (May and Baker), stearic acid (B.D.H.) and oleic acid (Schering Kahlbaum chemisch Fabrik);

(4) urea adducts with each of the previously mentioned fatty acids were prepared by the authors;

(5) 1 : 1 physical mixtures.

Finely powdered urea was thoroughly mixed with each of the previously mentioned fatty acids in a ratio of 1 : 1.

Apparatus

(1) Derivatograph, Paulik–Paulik and Erdey (3465), manufactured by MOM, Budapest, Hungary;

(2) Perkin–Elmer (U.S.A.) DSC-4 differential scanning calorimeter;

(3) Perkin–Elmer thermal analysis data station, "TADS";

(4) Perkin–Elmer TG S-2 thermogravimetric analyzer;

(5) Perkin–Elmer microprocessor temperature programmer system 4;

(6) Perkin–Elmer AD.2Z microbalance;

(7) Kofler microscope, Reichert (315602), Austria.

Procedures and calculations

Preparation of the adducts [10]

One gram of the fatty acid was dissolved in 25 ml methanol previously saturated with urea at room temperature. If necessary gentle heat was applied. Sometimes a few drops of chloroform were added to the solution till complete homogeneity was attained. The solution was allowed to stand at room temperature overnight. The crystals of the adduct were then filtered, washed with chloroform and air dried.

Differential thermal analysis (DTA)

About 0.1 g of the sample (urea, fatty acid, adduct or physical mixture) was accurately weighed. The sample was examined using Al_2O_3 (previously heated to 1200°C for 2 h) as a reference, under the following conditions: heating rate 20°C min^{-1}; sensitivity of the DTA galvanometer 1/10; temperature of the sample was raised linearly from ambient (20–25°C) up to 500°C within a time period of 25 min.

Differential scanning calorimetry (DSC)

Two to four mg of the sample were examined in a hermetically sealed aluminium crucible from 50°C to 150°C at a heating rate of 5°C min^{-1}. Nitrogen was used as the purge gas.

Thermogravimetry (TG) and derivative thermogravimetry (DTG)

Two to ten mg of the sample were examined starting from ambient temperature to 500°C. A heating rate of 20°C min^{-1} was generally used.

Determination of melting and boiling points

The Kofler microscope was used for the determination of the melting points of the fatty acids and the decomposition temperatures of their urea adducts [11]. Siwoloboff's method [12] was used for the determination of boiling points of liquid fatty acids.

Mathematical calculations

The heat of the reaction (ΔH) and purity determination were achieved as described previously [13].

RESULTS AND DISCUSSION

Collective DTA curves of urea, each fatty acid, its adduct and physical mixture with urea are presented in Figs. 1–7. The respective data for DTA reactions are shown in Table 1. Collective DSC, TG and DTG curves for urea and representatives of the adducts are shown in Figs. 8 and 9.

The different DSC reactions and their ΔH values are presented in Table 2 while the thermogravimetric reactions are shown in Table 3. Table 4 represents the decomposition temperatures of urea–*n*-fatty acid adducts.

Urea

Urea undergoes three endothermic reactions, the first of which is due to its melting. Its heat of fusion as determined by DSC was found to be 141.3 cal g^{-1}. The second and third endothermic reactions are due to biuret formation which undergoes the same reactions (Fig. 10). The melting of urea was preceded by another endothermic reaction which may be due to crystal transformation, having a ΔH value of 1.5 cal g^{-1}. From TG and DTG urea starts to decompose at 120°C, undergoing its main reaction which ends at 225°C with a weight loss of 73.2%. The purity of urea was determined successfully by calorimetric method and found to be 99.31% (Fig. 11).

TABLE 1

DTA reactions of urea, fatty acids, their adducts and 1:1 physical mixtures

Sample	First reaction				Second reaction				Third reaction				Fourth reaction				Fifth reaction			
	Nature	Start (°C)	Peak (°C)	End (°C)	Nature	Start (°C)	Peak (°C)	End (°C)	Nature	Start (°C)	Peak (°C)	End (°C)	Nature	Start (°C)	Peak (°C)	End (°C)	Nature	Start (°C)	Peak (°C)	End (°C)
Urea	Endo	112	140	175	Endo	175	283	360	Endo	360	430	470								
Butyric acid	Endo	120	187	290	Endo	290	403	496												
Adduct	Endo	110	140	173	Endo	173	265	338	Endo	338	409	440								
Physical mixture	Endo	100	121	138	Endo	138	220 271	335	Endo	335	422	470								
Caproic acid	Endo	140	232	297	Endo	297	415	500												
Adduct	Endo	80	97	118	Endo	118	137	162	Endo	162	274	336	Endo	336	417	470				
Physical mixture	Endo	74	86	109	Endo	109	126	156	Endo	156	225 270	322	Endo	322	419 433	470				
Lauric acid	Endo	41	48	182	Exo	262	288 308	330	Endo	330	373	435								
Adduct	Endo	109	147	180	Endo	180	280	336	Endo	375	418	450								
Physical mixture	Endo	30	50	106	Endo	120	140	172	Endo	172	273	300	Exo	300	313	365	Endo	365	400	424

Myristic acid	Endo	30	51	147	Exo	274	315	393	Endo	393	413	446								
Adduct	Endo	110	142	175	Endo	175	271	295	Exo	295	321	360	Endo	360	419 423	442				
Physical mixture	Endo	25	41	50	Endo	110	135	167	Endo	167	260	291	Exo	291	322	350	Endo	350	362 421	440
Palmitic acid	Endo	32	60	150	Exo	280	320	370	Endo	370	395	460								
Adduct	Endo	85	103	120	Endo	120	150	181	Endo	181	280	305	Exo	305	322	370	Endo	370	423	485
Physical mixture	Endo	40	60	110	Endo	110	130	162	Endo	162	268	300	Exo	300	325	350	Endo	350	373	398
Stearic acid	Endo	35	65	90	Exo	250	320 340	418												
Adduct	Endo	120	150	188	Endo	188	284	312	Exo	312	338	370	Endo	370	425	473				
Physical mixture	Endo	48	62	80	Endo	120	142	171	Endo	171	278	310	Exo	310	340	365	Endo	365	399	470
Oleic acid	Exo	80	140	230	Exo	230	281	305	Exo	305	335	388	Endo	388	421	462				
Adduct	Endo	102	140	180	Endo	180	270	308	Exo	308	335	360	Endo	360	383	416	Endo	416	434	450
Physical mixture	Endo	110	140	173	Endo	173	272	322	Exo	322	339	370	Endo	370	381	400	Endo	400	430	472

TABLE 2

DSC reactions of urea and its butyric, lauric, stearic and oleic acid adducts

Sample	First reaction				Second reaction			
	Start (°C)	Peak (°C)	End (°C)	ΔH (cal g^{-1})	Start (°C)	Peak (°C)	End (°C)	ΔH (cal g^{-1})
Urea	105	113.4	118.0	1.5	118.0	134.8	140	141.3
Butyric acid adduct	60	69.0	80.0	4.1	85.0	129.0	140	46.8
Lauric acid adduct	112	122.5	126.5	32.0	126.5	134.2	140	59.7
Stearic acid adduct					116.0	134.6	140	60.4
Oleic acid adduct	105	117.9	123.0	21.5	123.0	133.4	140	46.2

TABLE 3

Thermogravimetric reactions of urea and its butyric, lauric, stearic and oleic acid adducts

Sample	First reaction			Second reaction			Third reaction			Fourth reaction			Residue wt. (%)
	Start (°C)	End (°C)	Wt. loss (%)	Start (°C)	End (°C)	Wt. loss (%)	Start (°C)	End (°C)	Wt. loss (%)	Start (°C)	End (°C)	Wt. loss (%)	
Urea	120	225	73.2	225	250	4.5	250	340	19.3	340	400	3.0	
Butyric acid	40	100	4.9										
adduct	100	235	71.3	235	260	8.5	260	325	13.0	325	500	2.2	
Lauric acid adduct	104	235	83.0	235	260	5.2	260	322	11.0	322	360	0.7	
Stearic	41	140	1.0										
acid adduct	140	260	77.6				260	325	10.2	325	500	2.6	8.6
Oleic acid adduct	138	280	69.7				280	375	22.4	375	500	3.6	4.3

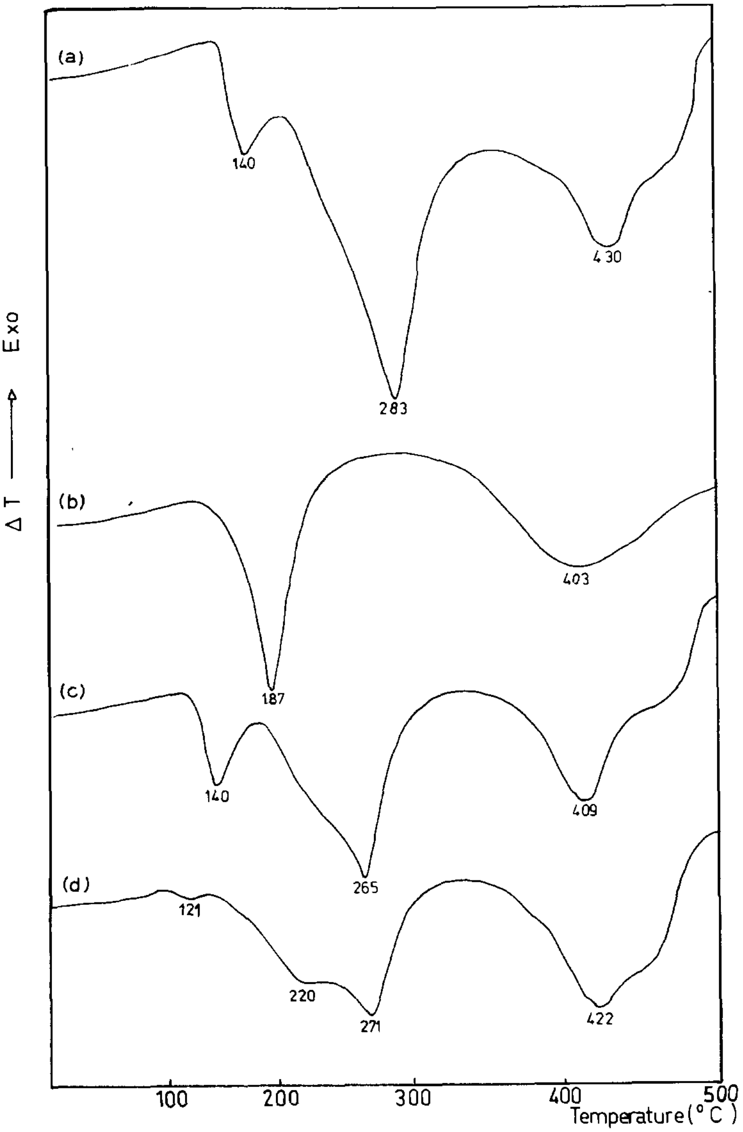

Fig. 1. DTA curves of (a) urea, (b) butyric acid, (c) their adduct, and (d) 1:1 physical mixture.

Fatty acids

The characterization of fatty acids was found to be possible through their DTA behaviour. Short-chain fatty acids which are liquids (butyric and caproic) exhibit two endothermic reactions, while starting from C_{12} (lauric acid) an exothermic reaction appears at 310–335°C.

In saturated fatty acids the first endothermic reaction is due to boiling in

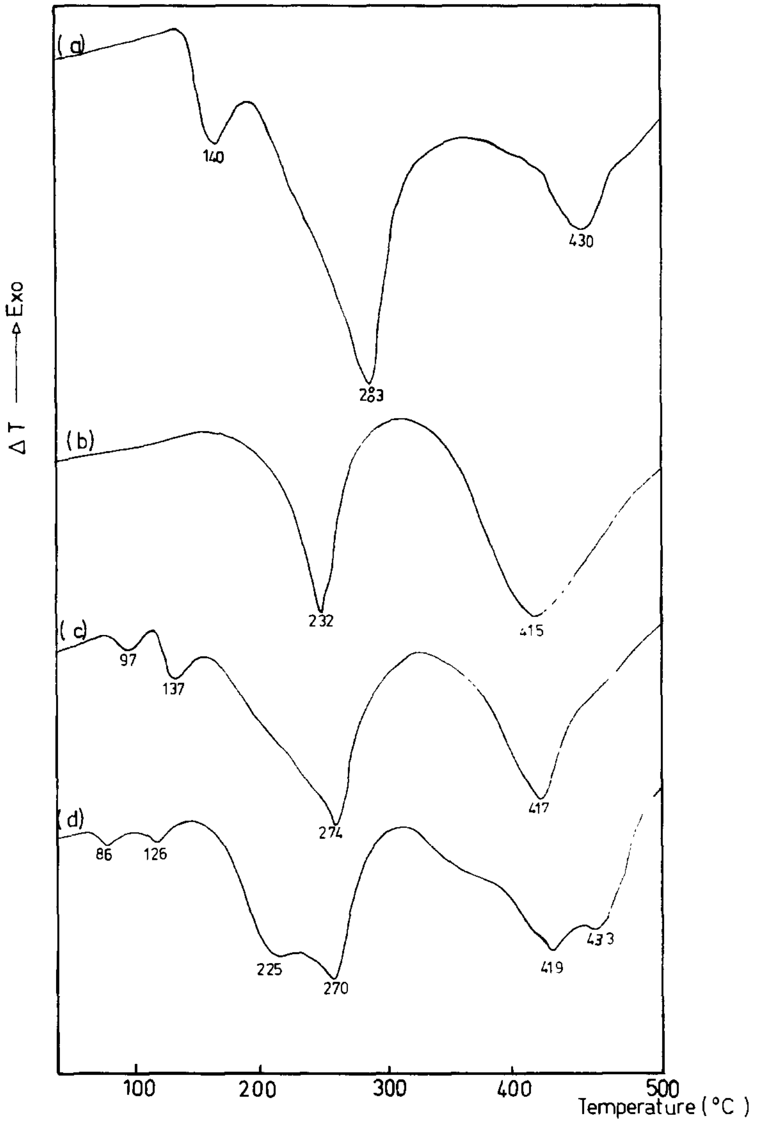

Fig. 2. DTA curves of (a) urea, (b) caproic acid, (c) their adduct, and (d) 1:1 physical mixture.

TABLE 4

Decomposition temperatures of urea–*n*-fatty acid adducts

Urea acid adduct	DTA incipient (°C)	TG incipient (°C)	DSC		Kofler (°C)
			Incipient (°C)	Peak (°C)	
Butyric	110	100	60	69	75
Caproic	80				81
Lauric	105	104	112	122.5	100
Myristic	102				105
Palmitic	85				115
Stearic	120	140	116	134	125
Oleic	102	138	105	118	113

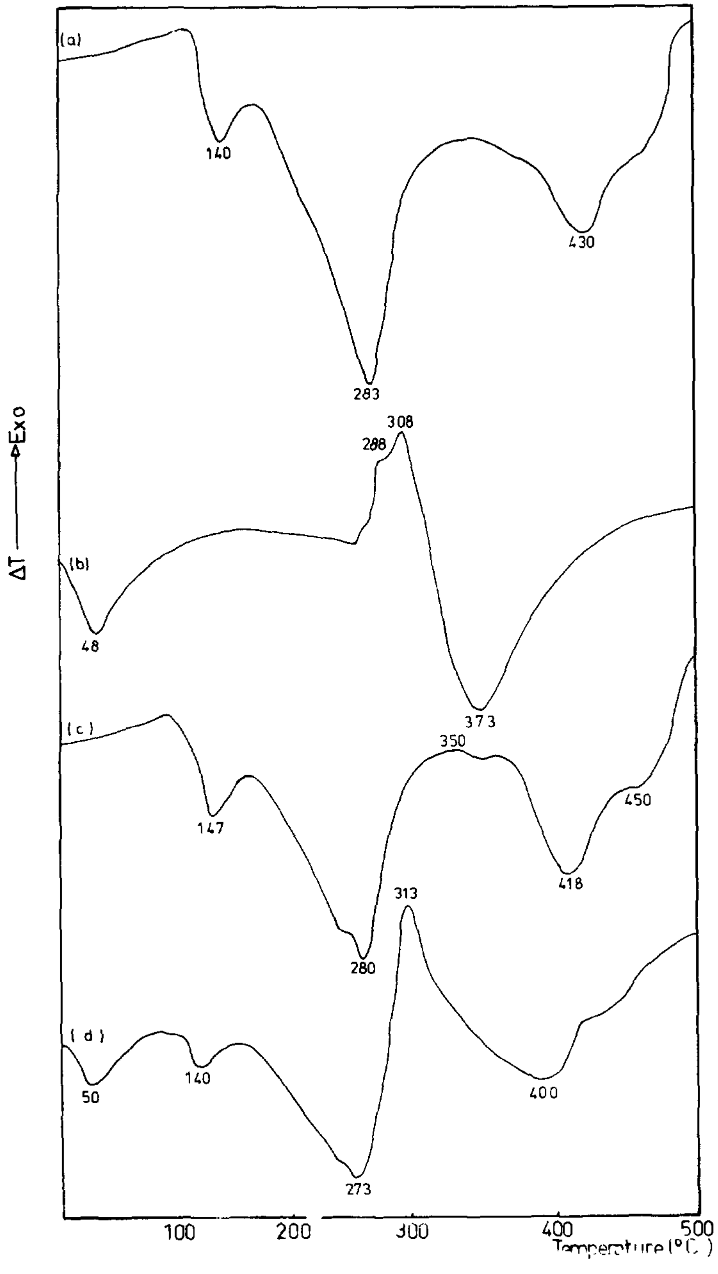

Fig. 3. DTA curves of (a) urea, (b) lauric acid, (c) their adduct, and (d) 1 : 1 physical mixture.

the case of liquids or melting in the case of solids.

The DTA of oleic acid ($C_{18}:1$) shows somewhat different behaviour. It undergoes three exothermic reactions and one endothermic reaction. The exothermic peaks are at 140, 281 and 335°C. The first two exothermic

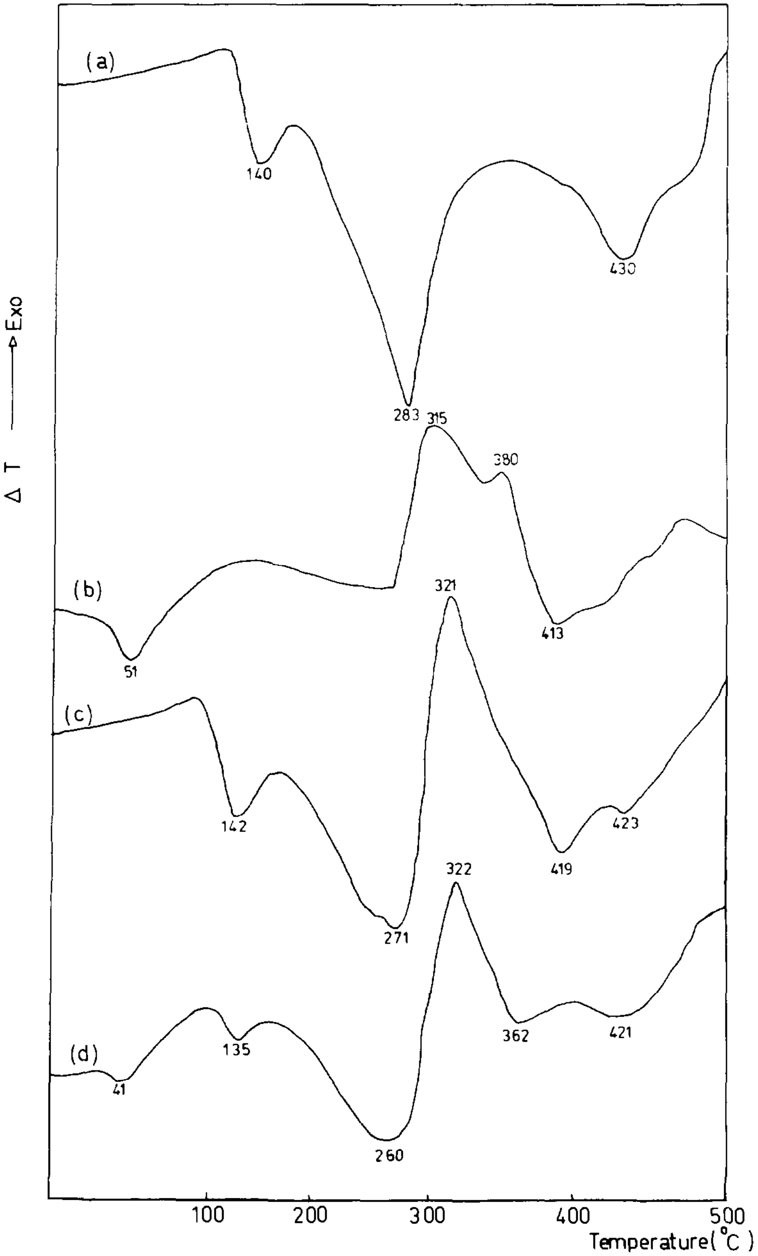

Fig. 4. DTA curves of (a) urea, (b) myristic acid, (c) their adduct, and (d) 1:1 physical mixture.

reactions are characteristic of unsaturation in oleic acid. This is probably due to either partial or complete saturation of the fatty acid by linking together of neighbouring chains prior to commencement of decomposition [14,15].

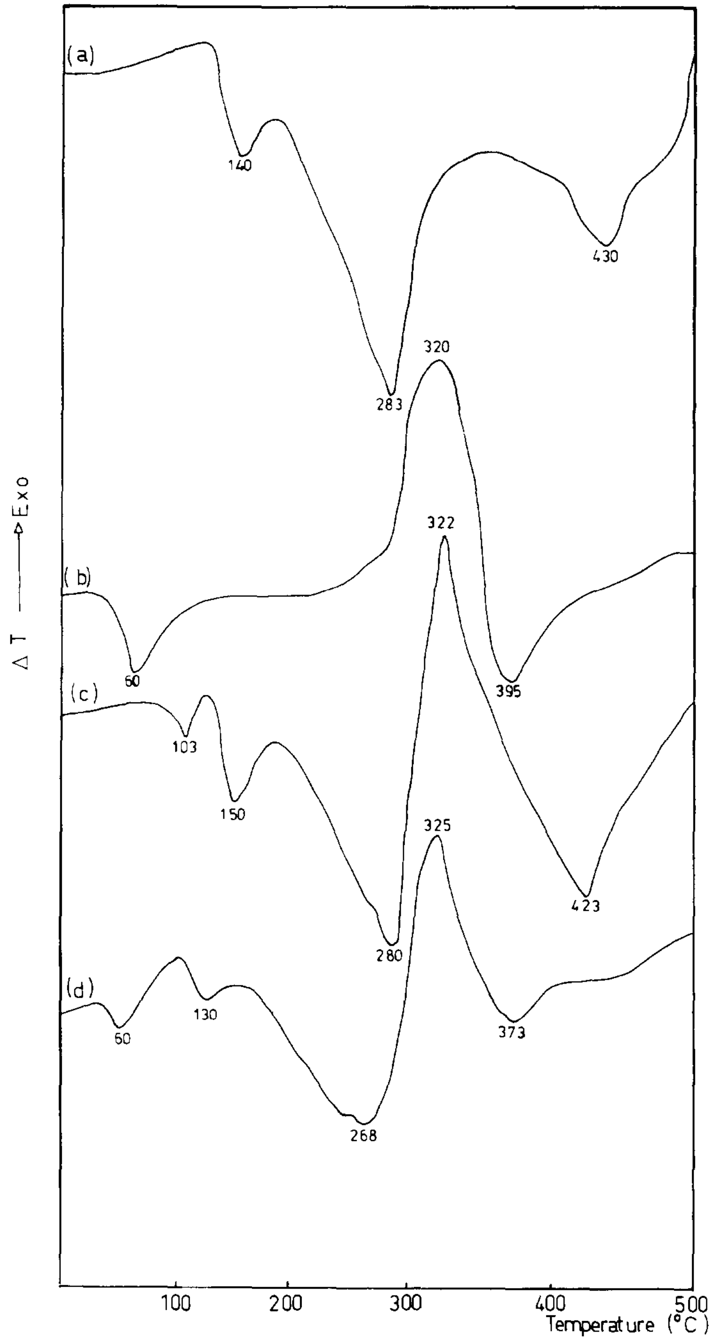

Fig. 5. DTA curves of (a) urea, (b) palmitic acid, (c) their adduct, and (d) 1:1 physical mixture.

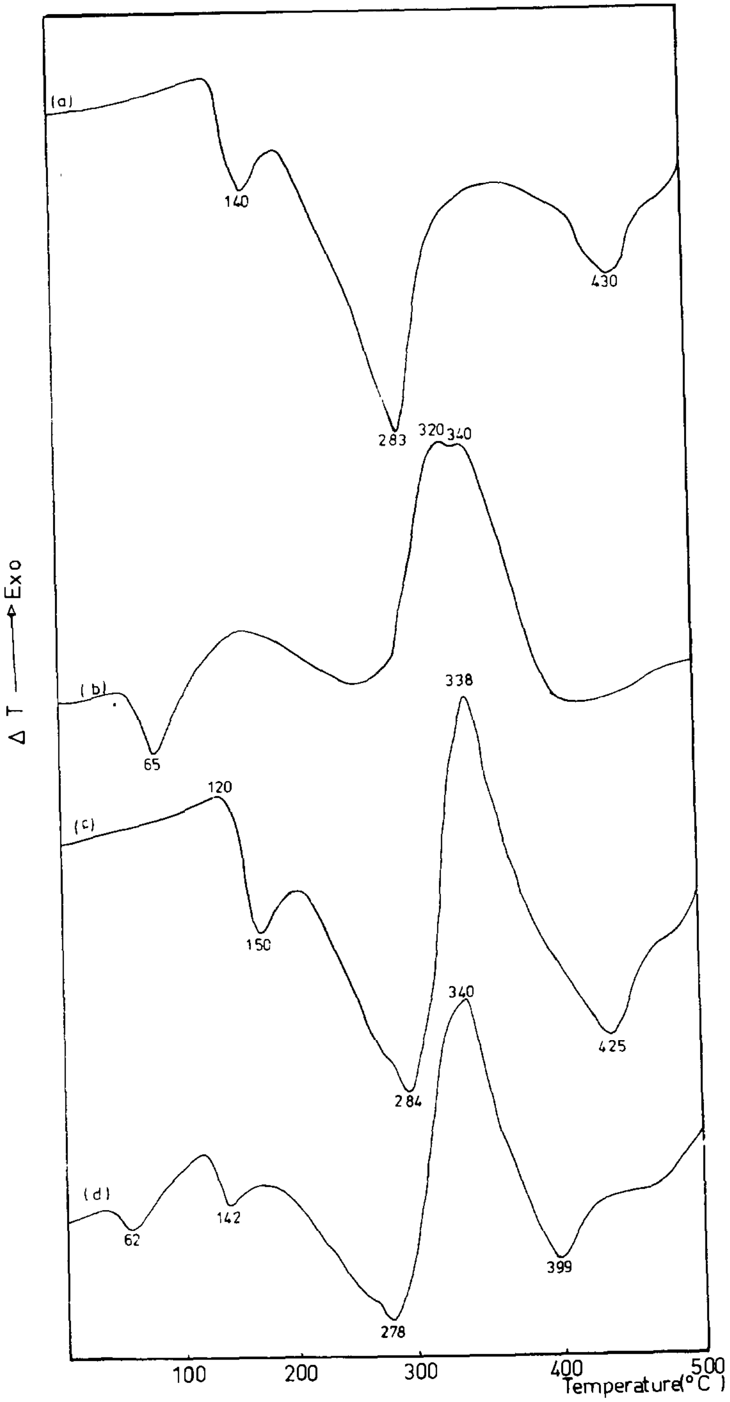

Fig. 6. DTA curves of (a) urea, (b) stearic acid, (c) their adduct, and (d) 1 : 1 physical mixture.

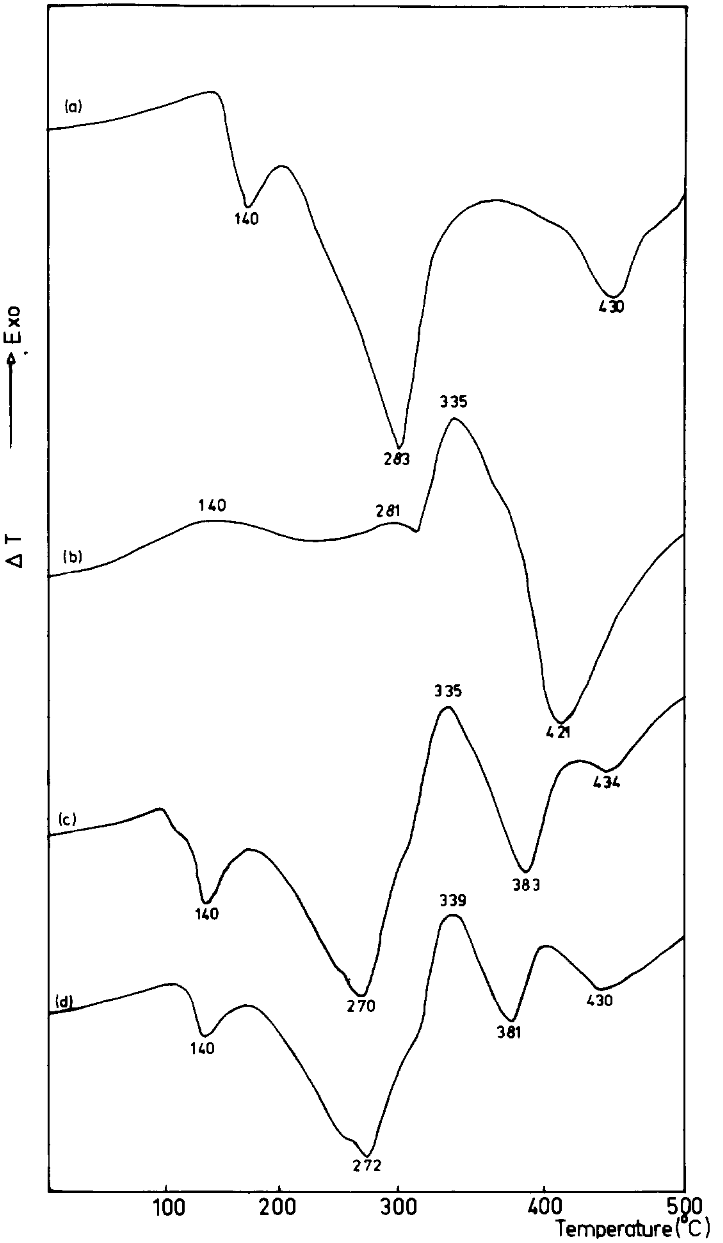

Fig. 7. DTA curves of (a) urea, (b) oleic acid, (c) their adduct, and (d) 1 : 1 physical mixture.

Table 5 presents the melting and boiling points of fatty acids as determined by DTA and other methods. The melting and boiling points increase with increase in chain length of fatty acid. In the case of oleic acid, boiling point determination by DTA was found to be unsuitable.

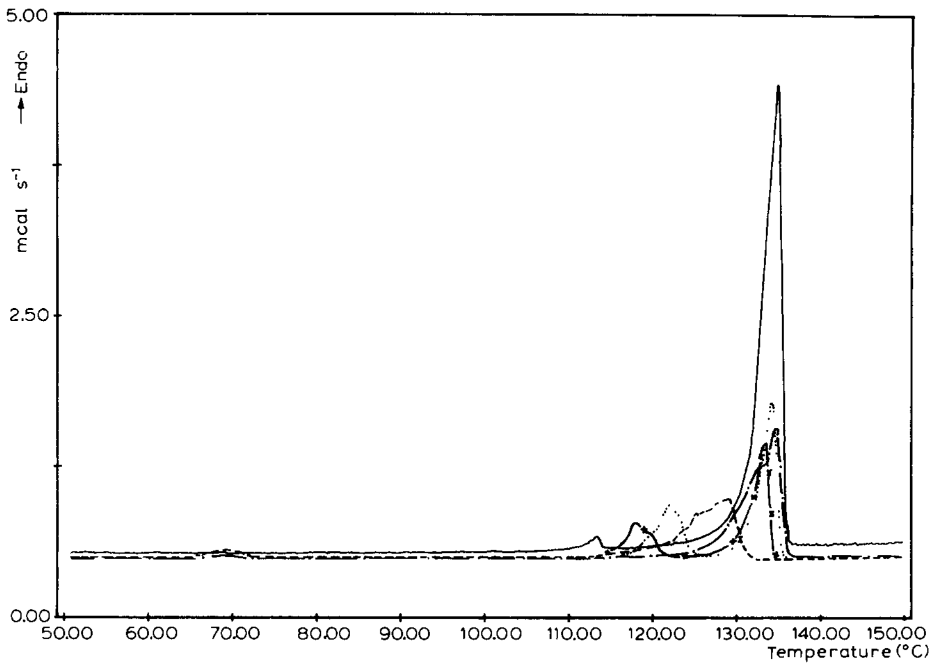

Fig. 8. Collective DSC curves for urea (———), butyric acid adduct (- - - - - -), lauric acid adduct (· · · · · ·), stearic acid adduct (· — · — ·), and oleic acid adduct (– × – × –).

Fatty acid–urea adducts

DTA of the adducts generally exhibits the first endothermic reaction of urea. This reaction includes at the start an inflection (in the case of lauric and oleic acid adducts at 127 and 121°C, respectively) or is preceded by a small endothermic reaction having its peak temperature in the case of caproic and palmitic acid adducts at 97 and 103°C, respectively. These

TABLE 5

Temperatures of melting, or boiling, points of fatty acids by different methods

Fatty acid	Lit. (°C)	DTA (°C)	Kofler or Siwoloboff's method (°C)
Butyric	162	187	161
Caproic	205	232	204
Lauric	44–48	48	43
Myristic	54	51	50
Palmitic	63	60	62
Stearic	69	65	67

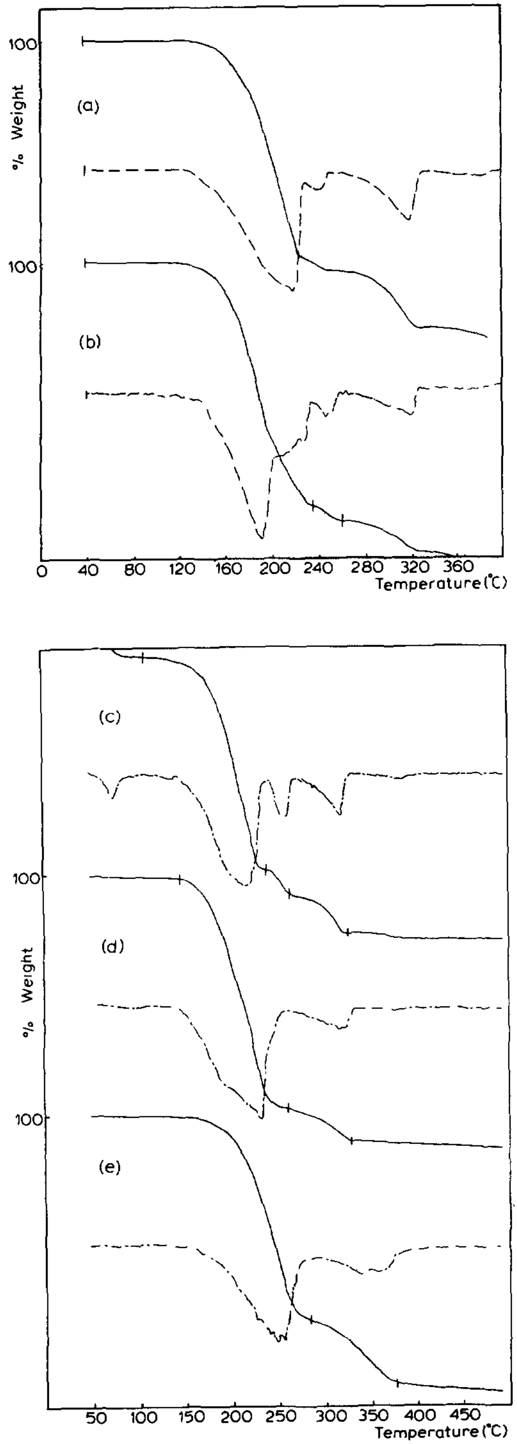

Fig. 9. TG (———) and DTG (- — - — -) curves for (a) urea, (b) lauric acid adduct, (c) butyric acid adduct, (d) stearic acid adduct, and (e) oleic acid adduct.

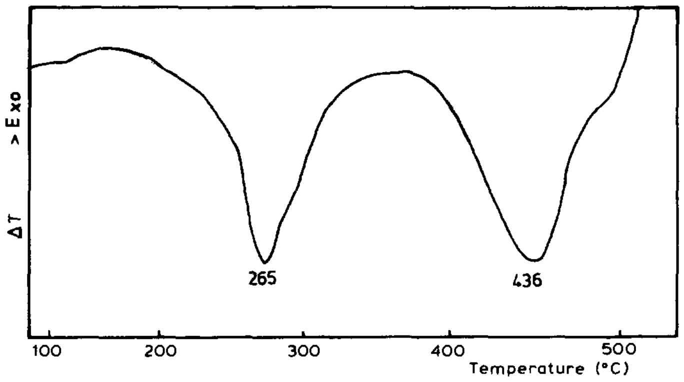

Fig. 10. DTA curve of biuret.

inflections or reactions indicate the decomposition of the adducts since they are not identified on examining the respective physical mixtures.

Other reactions characteristic of urea are identified on examining the adducts of caproic, lauric, myristic, palmitic, stearic and oleic acids (with peak temperatures at 274, 280, 271 and 423, 280 and 423, 284 and 425, 270 and 434°C, respectively).

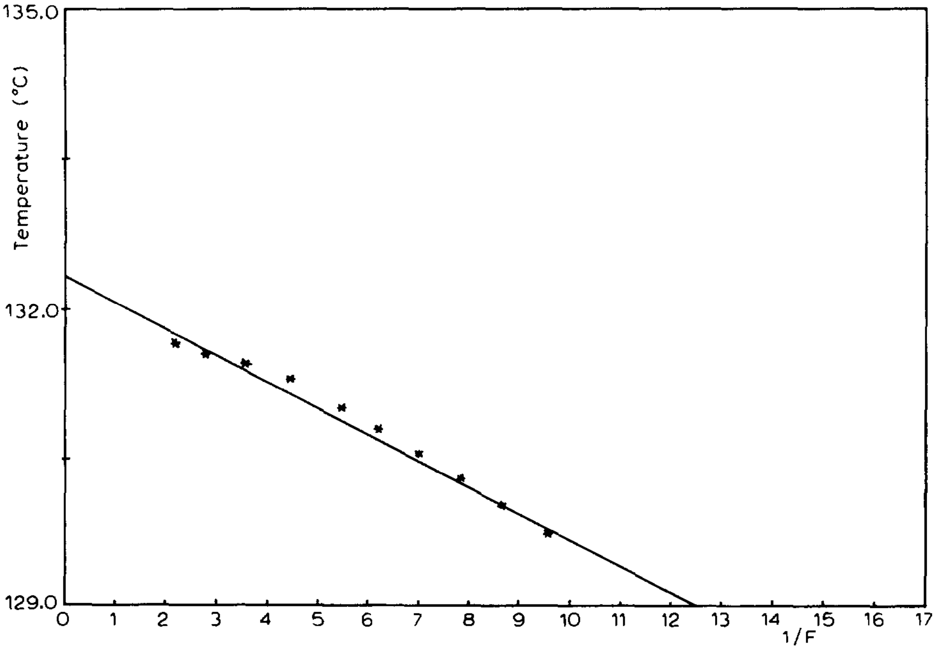

Fig. 11. Van't Hoff plot for urea (mol. wt. = 60.06). Peak from 105 to 140, PA from 129.92 to 133.65; heat of fusion = 8486.57 cal mol^{-1}; TM = 132.06; X-correction = 0%; purity = 99.31%. F = Fraction of the sample melted at the respective temperatures.

It is also found that the first endothermic reaction for the acid (boiling or melting) vanished on examining the respective adducts. This is attributed to inclusion of the acid within the urea lattice leading to a higher stability of the fatty acid than in the free state. On the other hand, some characteristic reactions of the fatty acids are still identified on examining their adducts such as the endothermic reactions with peak temperatures of 409, 417 and 419°C in the case of butyric, caproic and myristic acid adducts, respectively, and the exothermic reactions with peak temperatures of 321, 322, 338 and 335°C for myristic, palmitic, stearic and oleic acid adducts, respectively. This is attributed to the liberation of the acid from the urea lattice at high temperatures.

Also, there are some inflections characteristic of the adduct itself occurring in the range 250–260°C for short-chain fatty acid adducts and about 265°C for long-chain fatty acid adducts.

On DSC, the adducts of butyric, lauric and oleic acids undergo two endothermic reactions with peak temperatures at 69, 122.5 and 117.9°C (first reaction) and at 129, 134.2 and 133.4°C (second reaction), respectively. The heats of the reaction are 4.1, 32 and 21.5 cal g^{-1} (first reaction) and 46.8, 59.7 and 46.2 cal g^{-1} (second reaction), respectively.

Stearic acid undergoes one endothermic reaction with peak temperature at 134.6°C and a shoulder is observed at 132.3°C, indicating overlapping stages. ΔH was found to be 60.4 cal g^{-1}. The first reaction may be attributed to dissociation of the adduct while the second is due to melting of urea. The temperatures and ΔH values for these reactions increase with increase in chain length. The only exception is oleic acid adduct which has values lower than expected due to its unsaturation which hinders adduct formation. Although there is more or less similarity in the temperature of the DSC reaction between urea and its adducts, there is quite a large variation between the corresponding heat of reaction (ΔH_2). This may be due to crystal transformation of urea from the hexagonal to the tetragonal form on liberation of the guest molecule.

Thermogravimetric and derivative thermogravimetric investigations reveal that the first decomposition reaction is the main reaction in all cases with the largest weight loss (70–80%). In the case of butyric and stearic acid adducts this reaction is preceded by a small reaction which is attributed to loss of moisture. This is followed by smaller reactions, three in the case of urea, its butyric and lauric acid adducts, and two in the case of its stearic and oleic acid adducts. Thus the relation to urea and its various adducts is still evident.

The stability of the adducts is found to vary according to the guest molecule. For short-chain fatty acids (butyric and caproic) the adduct is less stable than both urea and the free fatty acid. This may be attributed to the small number of carbon atoms of the acid, being at the border of that required for adduct formation. For other fatty acids of longer chain length (lauric, myristic, palmitic and oleic) their adducts are more stable than the free fatty acid but less stable than urea. In the case of stearic acid its adduct is more stable than both urea and the free stearic acid.

Thus, it can be concluded that the stability of the fatty acid is increased by adduct formation with urea, stability increases with chain length and decreases with unsaturation.

The decomposition temperatures of the prepared adducts were determined using the Kofler microscope. In some cases these decomposition temperatures are correlated with the starting temperature of the first DTA reaction (lauric, myristic, stearic and oleic adducts).

Other parameters indicating decomposition of urea adducts are the incipient temperature of the first thermogravimetric reactions, starting and peak temperatures of the first DSC peak (Table 4). It is found again that the decomposition temperature increases with chain length. Oleic acid has its corresponding values less than stearic acid in spite of having the same chain length.

On examining the 1 : 1 physical mixture of urea and each of the fatty acids by DTA, the reactions characteristic of the respective adducts are more or less identified indicating adduct formation even on physical mixing. This was observed by Topchiev et al. [1] using *n*-paraffin adducts with urea. Also, in some cases characteristic reactions of the acids which disappear on examining the adducts are manifested in the physical mixtures. Such reactions are the melting reactions of the fatty acids and the exothermic reaction of lauric acid. This indicates that in such cases adduct formation on physical mixing occurs only to a certain extent. Increasing the ratio of urea to the fatty acid up to 9 : 1 also gave a very small endothermic peak, indicating that free fatty acid is still present.

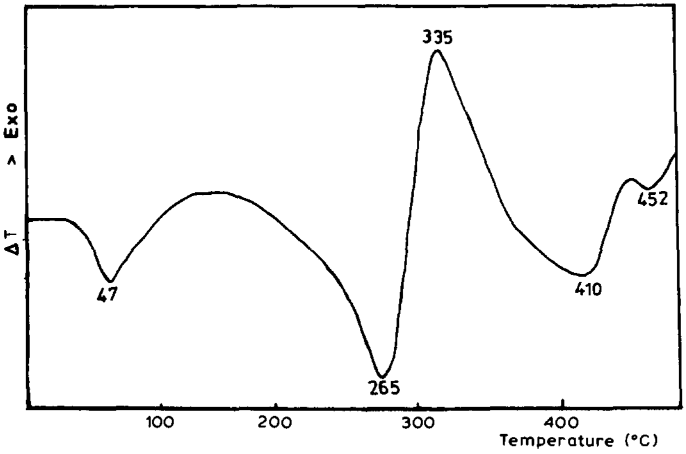

Fig. 12. DTA curve of 1 : 1 biuret and lauric acid.

In an attempt to determine whether the obtained results are peculiar to the adducts of fatty acids with urea and not to their reactions with biuret, DTA examination of a mixture of lauric acid and biuret was carried out. It was found to be not similar to that of the adduct but as the physical mixture in which the characteristic reactions of the acid are manifested (Fig. 12). This emphasizes that the previous results are peculiar to the adducts of fatty acids with urea and not to their reaction with its decomposition product, biuret.

ACKNOWLEDGEMENT

The authors express their thanks to Dr. Willy Surer, Scientific Staff, Perkin–Elmer, for his help in carrying out the DSC, TG and DTG scans.

REFERENCES

1 A.V. Topchiev, L.M. Rozenberg, N.A. Nechitalio and E.M. Terent'eva, Dokl. Akad. Nauk SSSR, 98 (1954) 223.
2 A.V. Topchiev, L.M. Rozenberg, N.A. Nechitalio and E.M. Terent'eva, Zh. Neorg. Khim., 1 (1956) 1185.
3 H.G. McAdie, Can. J. Chem., 40 (1962) 2195.
4 G.N. Chekhova and Yu. A. Dyadin, Deposited Doc. VINITI, 19 (1976) 1644.
5 V.A. Logvinenko, O.V. Gegola, G.N. Chekhova and Yu. A. Dyadin, Tezisy Dokl. Sovesch. Kinet. Mekh. Khim. Reukts. Tuerd. Tele, 1 (1977) 150.
6 A.A. Gundyrev, L.P. Kazakova, M.V. Karaiboy and L.N. Tarasova, Khim. Tekhnol. Topl. Masel, 5 (1977) 13.
7 J. Chatani, H. Anraku and Y. Taki, Mol. Cryst. Liq. Cryst., 48 (1978) 219.
8 P. Schuster, Thermochim. Acta, 3 (1972) 485.
9 A.I. Vogel, Practical Organic Chemistry, Longmans Green and Co., 3rd edn., 1967, p. 442.
10 J.M. Moreno and A.V. Roncevo, in H.A. Boekenoogen (Ed.), Analysis and Characterization of Oils, Fats and Fat Products, Vol. I, Interscience, London, New York, Sydney, 1964, p. 95.
11 H.B. Knight, L.P. Witnauer, J.E. Coleman, W.R. Noble and D. Swern, Anal. Chem., 24 (1952) 1331.
12 A.I. Vogel, Practical Organic Chemistry, Longmans Green and Co., 3rd edn., 1967, p. 85.
13 F.I. Khattab, Thermochim. Acta, 61 (1983) 253.
14 H.E. Rost, Fette, Seifen, Anstrichm., 64 (1962) 427.
15 Mi Jakawa and H. Nomizu, Fette, Seifen, Anstrichm., 64 (1962) 593.