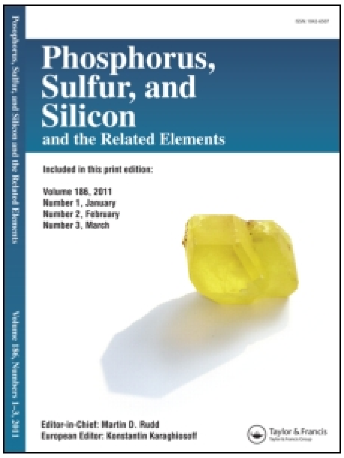

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Synthesis and Characterization of the New 1-Arylsulfonyl-2-Nitroethanes, Part II

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Synthesis and Characterization of the New 1-Arylsulfonyl-2-Nitroethanes, Part II

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The thermal behaviour of 2-nitro-1-phenyl-1-phenylsulfonylethane and its derivatives was studied by using the combined dynamical thermal analysis method. Some thermochemical and kinetical characteristics of these solid organic compounds were determined for the first time. An attempt to analyze the effects of both the physical and chemical structure of the corresponding samples on these characteristics was made.

Keywords Nitrosulfones; thermal analysis method; thermochemical and kinetical characteristics

INTRODUCTION

The 1-aryl-1-arylsulfonyl-2-nitroethanes are solid, crystalline compounds that have previously been synthesized by the nucleophilic addition reaction of arenesulfinic acids to 2-nitrostyrene and its derivatives.[1] Significant number of these compounds have been found to exhibit some pesticidal, fungicidal, and acarizidal activity and psychotropic effects and thus can serve as starting materials for the preparation of biologically-active substances. The determination of some thermal characteristics of these compounds and their relation to the corresponding chemical and physical structures seems to be an interesting task from the theoretical point of view. On the other hand, the scientific aspects concerning the applied organic chemistry are also important in terms of predicting some properties of these compounds and their possible practical application.

No systematic studies on the thermal behavior of these compounds within a wide temperature interval have been found in the literature so far. Thermal analysis, however, is believed to provide an additional

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information about the strength of the corresponding chemical bonds, associated with their thermal and thermooxidative stability and reactivity. Thermal analysis studies have been conducted with organic nitrocompounds, particularly, aliphatic ones in gaseous phase, under isothermal conditions predominantly.[2] Some research on the processes of gas release from nitrocompounds containing other functional groups and subjected to thermal treatment at high heating rates (20 K/s) has also been carried out.[3–6] Such studies, conducted in condensed phase are considered to be rare.[7] Based on the results obtained, most of the nitrocompounds are believed to decompose at significantly higher rate in condensed phase, due to the catalytic effects of both the nitro- and nitrosogroups present. The effects of some substituents on the melting temperature and the explosive properties of the corresponding nitrocompounds have also been discussed by employing the thermal analysis data.[2–7]

Without doubt, a number of specific features associated with the behavior of the nitrocompounds subjected to thermal degradation are of a significant interest for the theory of monomolecular reactions. The possibilities of degradation, taking place by two parallel mechanisms, i.e., radical and molecular, and depending on both the molecular structure and experimental conditions, are among these features. Establishing the kinetics and mechanism of thermal degradation of any nitrocompound would be of significant importance for the theory of the combustion of one-component systems.

Therefore, the objective of this work was to study the thermal behavior of newly-synthesized solid organic compounds within a wide temperature range and to determine some of the corresponding thermochemical and kinetical parameters.

RESULTS AND DISCUSSION

The thermal analysis scans obtained within the temperature interval of 20° to 600°C showed that the compounds under study had similar thermal characteristics and thus enabled the joint and complex analysis of the corresponding data. The differences in the physical structure and the chemical composition of these compounds corresponded to pronounced differences in the mode of their thermal behavior. The thermal analysis scans of the 1-aryl-1-arylsulfonyl-2-nitroethanes exhibited several very similar stages, reflected in the course of the curves and accompanied by the corresponding thermal effects. The observed effects can be subdivided as follows: melting of the crystalline phase, which implied the determination of the melting temperature T_m and the corresponding thermodynamical parameters ΔH_m and ΔS_m, (Table I,

TABLE I Thermal and Kinetic Characteristic for 1-Aryl-1-arylsulfonyl-2-nitroethanes

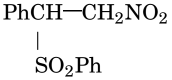
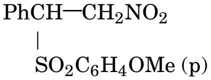
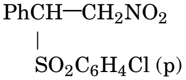
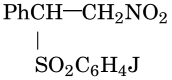
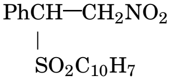
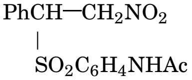
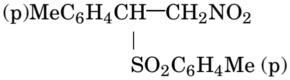
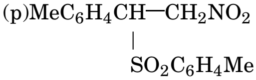
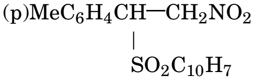
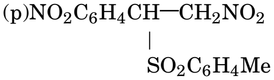
No.			T_T °C	H_m J/mol	S_m J/mol · deg	E_a kJ/mol	Z S^{-1}
1	 $\underset{SO_2Ph}{\underset{\vert}{PhCH}}-CH_2NO_2$	(air) (nitrogen)	175 175	376.0	0.84	244.5	$1{,}9.10^{24}$
2	 $\underset{SO_2C_6H_4OMe\ (p)}{\underset{\vert}{PhCH}}-CH_2NO_2$		145	253.0	0.61	234.1	$3{,}6.10^{22}$
3	 $\underset{SO_2C_6H_4Cl\ (p)}{\underset{\vert}{PhCH}}-CH_2NO_2$		135	225.0	0.56	198.5	$3{,}7.10^{19}$
4	 $\underset{SO_2C_6H_4J}{\underset{\vert}{PhCH}}-CH_2NO_2$		140	328.0	0.79	225.7	$3{,}8.10^{22}$
5	 $\underset{SO_2C_{10}H_7}{\underset{\vert}{PhCH}}-CH_2NO_2$		135 150	219.5	0.52	295.1	$9{,}6.10^{29}$
6	 $\underset{SO_2C_6H_4NHAc}{\underset{\vert}{PhCH}}-CH_2NO_2$		90 165	...	...	...	...
7	 $(p)MeC_6H_4\underset{SO_2C_6H_4Me\ (p)}{\underset{\vert}{CH}}-CH_2NO_2$		80 100	184.4	0.49	159.4	$5{,}4.10^{14}$
8	 $(p)MeC_6H_4\underset{SO_2C_6H_4Me}{\underset{\vert}{CH}}-CH_2NO_2$		105 115	142.0	0.37	194.4	$7{,}0.10^{18}$
9	 $(p)MeC_6H_4\underset{SO_2C_{10}H_7}{\underset{\vert}{CH}}-CH_2NO_2$		120 135	150.0	0.38	200.6	$2{,}9.10^{19}$
10	 $(p)NO_2C_6H_4\underset{SO_2C_6H_4Me}{\underset{\vert}{CH}}-CH_2NO_2$		175	192.5	0.43	140.0	$1{,}7.10^{13}$

Figure 1) the initial degradation, expressed by some parameters characterizing the relative thermostability, such as T_0, $T_{10\%}$, $T_{25\%}$; the apparent activation energy E_A and the corresponding pre-exponential factor Z; the temperatures of the maximum and the endset of the first exothermal effect and the corresponding mass losses, evaluated by the parameters T_{lexo}, T_{kpl}, ΔM_{lexo}; the second stage of degradation, estimated by the parameters $T_{50\%}$ R_{400}, and the temperatures of the accompanying thermal effects; and the third stage of degradation (the parameters T_{kp} and R_{600}). The corresponding stoichiometric calculations based on the TG curves were made for every stage of the process in order to estimate the probable overall mechanism of thermal degradation (Figure 1). To

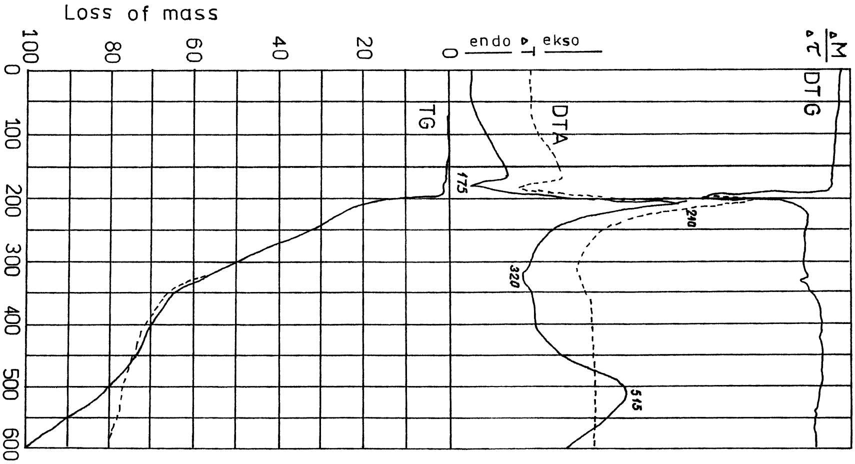


FIGURE 1 Thermoanalytical curves (DTA, TG, DTG) of 2-nitro-l-phenyl-l-phenylsulfonylethane in air atmosphere (-) and under nitrogen(---) at heating rate of 6°C/min.

this purpose, the IR spectra of the residues obtained after the initial degradation to the temperature of 230°C were compared to the spectra of the corresponding starting (initial) compounds.

Compound 1 was selected as a reference one in order to compare the thermal behavior of the organic chemicals studied. The corresponding DTA curve 1 showed a well pronounced endothermal effect of melting at 175°C (Figure 1) with the enthalpy of melting, determined experimentally $\Delta H_m = 376\ J \cdot mol^{-1}$ (Table I). Immediately following the melting, a fast exothermal-autocatalytic process took place within the temperature interval of 185 to 220°C with the corresponding maximum at 215°C and this was accompanied by the mass loss $\Delta M_{iexo} = 22\%$. The apparent activation energy E_A as determined experimentally was found to be $244.5\ kJ \cdot mol^{-1}$ (Table I). The comparison of the IR spectrum of the starting compound (Figure 2, curve 1) with that of the residue obtained after its heating to 230°C (Figure 2, curve 2) indicated disappearance of the bands assigned to the nitrogroup at 1540 $cm^{-1}(\nu_{as})$ and 1370 cm^{-1} (ν_s). The stoichiometric calculations based on the mass losses within this temperature interval, following the first '*step*' in the TG curve also supported the assumption for the elimination of the nitrogroup $-NO_2$, more particularly, the radical fragments CH_3 and NO_2. For example, the IR spectrum of the sample, subjected to preliminary heating, showed also that, apart from the nitrogroup, the bands at 3000–2800 cm^{-1} assigned to methyl groups disappeared, too. The intensity of the bands,

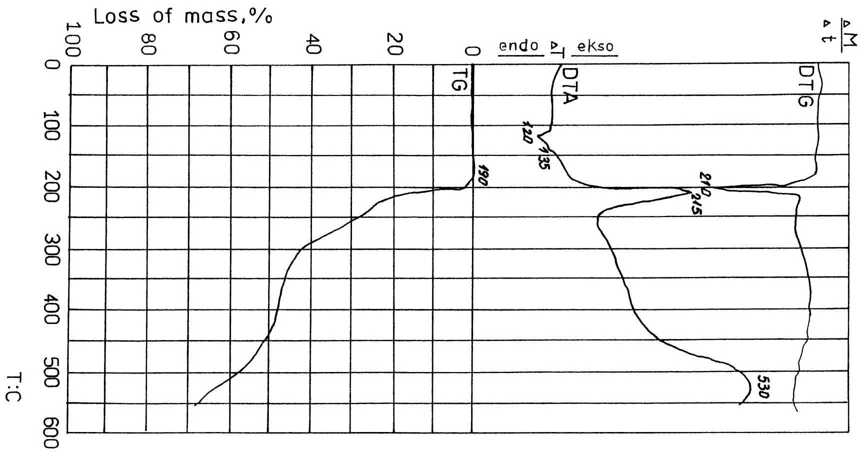


FIGURE 2 IR spectrum of 2-nitro-1-phenyl-l-phenylsulfonylethane. (-) the starting material; (---) at the starting material after 230°C.

corresponding to the sulfonyl groups at 1300, 1140, and 1070 cm^{-1}, was decreased as a result of this initial thermal treatment. Following the initial heating in air atmosphere, the IR spectrum of compound 1 showed some new weak bands at 1700–1600 cm^{-1} assigned to the C—O—C bonds. Heating the sample in nitrogen atmosphere under the same conditions (Figure 1, curve 2) did not significantly change the thermal characteristics and the corresponding parameters for the first stage of degradation and this confirmed the initial assumption for the course of the process.

The second stage of the thermal decomposition was found to take place in the temperature interval of 230–400°C and occurred at slower average rate with the mutual offset of the endothermal and exothermal processes. Based on stoichiometric calculations from the TG data, a decomposition process accompanied by the elimination of sulfopheyl and aliphatic fragments can be assumed.

The third stage of degradation within the range of 400–600°C was characterized by a wide exothermic *plateau* with a maximum at 515°C and was associated with the oxidation processes of the possible combustion of arene residue fragments. This was supported by the lack of these effects in nitrogen atmosphere.

The comparative studies on the thermal behavior of the compound 1 derivatives showed that their melting temperatures were within the range of 100–175°C (Table I). Single endothermal melting peaks were registered with compounds 1–4 and relatively high values of the corresponding enthalpies ΔH_m were found (Table I). Twin melting peaks

TABLE II Thermal Characteristics the Compounds Studied

No.	Compounds	T_0 °C	T_{lEXO} °C	M_{lEXO} %	$T_{kp.lEXO}$ °C	$T_{10\%}$ °C	$T_{25\%}$ °C	$T_{50\%}$ °C	$T_{kp.}$ °C	R_{400} %	R_{600} %
1	$PhCH—CH_2NO_2$ (air) $\vert$	180	215	25	225	205	225	295	600	28.0	0
	SO_2Ph (nitrogen)	180	210	25.5	225	200	225	290	600	27.0	18.0
2	$PhCH—CH_2NO_2$ $\vert$ $SO_2C_6H_4OMe$ (p)	190	225	25	235	215	235	300	580	28.0	0
3	$PhCH—CH_2NO_2$ $\vert$ $SO_2C_6H_4Cl$ (p)	175	205	25	230	200	220	305	585	28.5	0
4	$PhCH—CH_2NO_2$ $\vert$ $SO_2C_6H_4J$	180	200	20	225	205	245	305	600	27.5	2.5
5	$PhCH—CH_2NO_2$ $\vert$ $SO_2C_{10}H_7$	185	215	20	220	215	240	340	600	42.0	13.0
6	$PhCH—CH_2NO_2$ $\vert$ $SO_2C_6H_4NHAc$	170	195	30	210	190	215	340	600	43.0	3.0
7	(p)$MeC_6H_4CH—CH_2NO_2$ $\vert$ $SO_2C_6H_4Me$ (p)	180	210	21	220	215	230	310	570	36.0	9.0
8	(p)$MeC_6H_4CH—CH_2NO_2$ $\vert$ $SO_2C_6H_4Me$	170	215	24	220	210	225	300	600	33.0	14.0
9	(p)$MeC_6H_4CH—CH_2NO_2$ $\vert$ $SO_2C_{10}H_7$	195	215	20	220	210	240	455	600	52.0	18.0
10	(p)$NO_2C_6H_4CH—CH_2NO_2$ $\vert$ $SO_2C_6H_4Me$	180	210	10	210	210	260	420	600	52.0	15.0

were registered with 2-nitro-1-phenyl-1-arylsulfonylethanes, containing substituents in the sulfophenyl fragment. DTA curves of all of the compounds studied showed a strong and sharp exothermal effect, following the melting. The onset of these peaks was registered at 170–195°C, with a maximum at 195–225°C and endset at 210–235°C. The calculated mass losses, associated with these effects varied between 10 and 30 mass percent. The stoichiometric calculations were found to be in a very good agreement with the assumption that, as mentioned above, the nitrogroups and methyl groups were eliminated as radical fragments. In fact, this correlation, based on the radical mechanism of elimination, was better than that obtained with the assumption of the so-called molecular mechanism of degradation with the elimination of nitrous acid. The activation energy and the preexponential factor as kinetical parameters of the degradation process for this stage had relatively high values, i.e., between 194.4 and 295 kJmol^{-1} and 2.6 × 10^{18} and 9.6 × 10^{29} s^{-1}, respectively, for the most of the compounds studied. This suggested a radical mechanism of degradation. The only exception in this respect was compound 6, in which the elimination of the nitrogroup was accompanied by the hydrolytic cleavage of the acyl group and this, unlike the rest of the compounds, caused the partial offset of the exothermal elimination of the nitrogroup. The first stage of the thermal degradation of compound 6 occurred at lower temperatures (170–220°C) and was accompanied by the highest mass loss (30%). With compounds 2, 3, and 4, containing methoxy groups and halogens as substituents, some decrease of the initial thermal stability as compared to compound 1 was also observed. This was probably due to the higher susceptibility of compounds, containing these substituents towards oxidative degradation. Compounds 5 and 9 contained cycloaliphatic ring systems as structural fragments and this probably caused the observed increase of most of the characteristic temperatures and the higher overall thermal stability.

The second stage of the thermal degradation at 230–400°C was characterized by pronounced similarity in the thermal curves for the compounds studied. The rates of the thermal degradation processes changed but, on the whole, were found to be lower than those of the first stage. Therefore, some cross-linking effects and reactions were considered possible. The thermal characteristics of compound 9 provided the most supportive information in this respect (Figure 3).

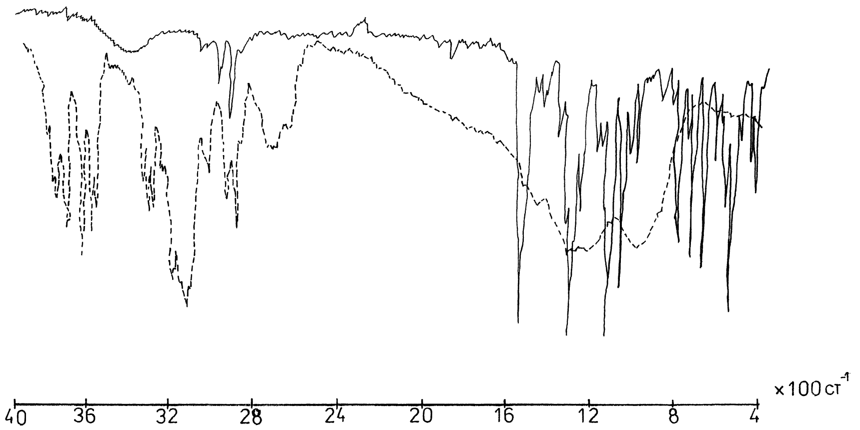


FIGURE 3 Thermoanalytical curves (DTA, TG, DTG) of 2-nitro-l-(1-naftylsulfonil)-1-(4-tolyl)ethane in air atmosphere at heating rate of 6°C/min.

Regardless of some slight decrease in the apparent activation energy E_A for the first stage of the thermal degradation of this compound, the parameter $T_{50\%}$ had higher value by, approximately, 100°C as compared to the rest of the compounds studied. The stoichiometric calculations supported the assumption for some additional *build-up* of both the sulfophenyl and aliphatic fragments in the molecules of this compound.

The complexity of the thermal degradation reactions caused some obscurity in the course of the corresponding curves which was also due to the mutual offset of the accompanying endothermal and exothermal reactions. The temperature region of 310–340°C was the only one in which the endothermal breakage of the chemical bonds predominated.

The last stage of the thermal degradation at 400–600°C for all of the compounds studied was associated with the combustion of the arene residual fragments. Accordingly, wide exothermal *plateaus* were observed within the temperature interval of 450–600°C. Some of the samples burned out completely, whereas, with others, some solid residues were formed at the end of analysis. Lack of these effects was, indeed, observed with the experiments in nitrogen atmosphere.

EXPERIMENTAL

Methods

Infrared (IR) spectra were recorded for all samples in order to initially identify the compounds. IR spectra were also obtained for a number of the secondary products, formed by heating the samples under the standard conditions till the endset of the first exothermal effects registered on the DTA curves. In both cases, KBr pellets were used for the sample preparation and the IR spectra were recorded by employing the Specord IR-75 instrument (Germany).

Combined Dynamical Analysis

The Analyses were performed on MOM Derivatograph (Budapest, Hungary) instrument under the following conditions: temperature range within 20–600°C, heating rate of 6°C/min, initial sample mass 100 ± 0.5 mg, metalloceramic crucible of internal diameter 12.5 mm as a sample holder, and α-Al_2O_3 as a standard in both the air (static) and nitrogen gas flow (171/h) atmosphere. The melting temperatures of the crystalline phases (T_{in}) as well as the initial temperatures of thermal degradation (T_0), the temperatures corresponding to 10, 20, and 50% mass loss, and the end of degradation (T_{10}, T_{25}, T_{50}, T_{edn}, respectively) were determined from the termogravimetric scans. The corresponding solid residues at 400 and 600°C (R_{400} and R_{600}) were also evaluated. By using the graphic intergation based on the sample weight method, the areas, related to the melting endothermic effects for the compounds studied, were calculated. β-Naphthol (p.a.) was the compound selected as a reference sample in order to determine the melting heats and endtropies (ΔH and ΔS). On the basis of the thermogravimetric scans, the parameters mentioned above and the relevant software, both the apparent activation energies (E_A) and preexponential factors (Z) of the *Arrhenius* equation for the rate constants, corresponding to the initial step of thermal degradation were also calculated. The results were statistically evaluated by calculating the corresponding correlation and dispersion coefficients and other parameters by using the least square method.

CONCLUSIONS

The thermal degradation studies of eight solid crystalline organic compounds of similar structure and composition have been conducted within the temperature interval from 20 to 600°C. The basic thermal characteristics such as temperatures, enthalpies and enthropies of melting are determined by employing the combined dynamical thermal analysis method. Other parameters, characterizing different stages of the thermal degradation process such as mass loss, temperature and some kinetical characteristics are also found. Some suggestions, concerning the likely overall mechanisms of the thermal degradation of the compounds under study and related to their chemical structures, are made.

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