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THERMAL STABILITY OF ALKYL 2,4-DINITROBENZENESULPHONATES

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Abstract—A study of the thermal stability of some alkyl 2,4-dinitrobenzenesulphonates is reported; some suggestions are made about possible mechanisms for the pyrolytic decomposition. The esters that possess straight-chain alkyl groups are much more stable than the corresponding iso-alkyl compounds. An evaluation of the methods of preparation of the esters is included and two new compounds, n-amyl and isoamyl 2,4-dinitrobenzenesulphonate, are described.

THE alkyl 2,4-dinitrobenzenesulphonates are valuable quaternizing agents,[1-6] but little is known about their thermal stability. Thermal decomposition of alkyl esters of aromatic sulphonic acids is known to give parent acid and olefin (or some polymerization product of the latter),[7-9] but when heated in certain organic solvents, alkylation of the nucleus occurs.[10,11]

Three methods for the preparation of alkyl 2,4-dinitrobenzenesulphonates have been described;[3,12,13] Chadbourne and Nunn[13] reported comparative data for these. In the present work, their method involving the interaction of 2,4-dinitrobenzenesulphonyl chloride and sodium alkoxide was not found to give consistent yields, even minute traces of moisture having a deleterious effect upon the reaction. Furthermore, the products contained a small amount of water soluble impurity (sodium salt or free acid) which could only be removed by extraction of the ester with chloroform. Using their second method,[13] whereby hydrogen chloride is removed between the sulphonyl chloride and the alcohol by means of 2,6-lutidine, we found that meticulous drying of the alcohol was not necessary and indeed with some of the higher esters, the use of undried alcohol gave only a slight decrease in yield. The products obtained were purer and the process was much more amenable to large-scale working.

Accordingly, an attempt was made to apply this second method to the preparation

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[12] A. I. Kiprianov and A. I. Tolmachev, *J. Gen. Chem. USSR* **27**, 553 (1957).

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of methyl and ethyl 2,4-dinitrobenzenesulphonates. No methyl ester was obtained, but a small amount of quaternary salt was isolated from a reaction mixture; additional small scale experiments showed that 2,6-lutidine was readily quaternized by methyl 2,4-dinitrobenzenesulphonate even at 0°, there being a considerable temperature rise (10–15°) despite ice-bath cooling. Losses due to quaternization of 2,6-lutidine in the preparation of ethyl 2,4-dinitrobenzenesulphonate were small and yields of 55% were possible, which compared favourably with those we obtained by the alkoxide method. The higher alkyl esters are progressively less reactive. Thus, no difficulties were experienced in using the lutidine method to obtain n-amyl and isoamyl 2,4-dinitrobenzenesulphonates in 62% and 61% yield respectively.

As long ago as 1920, Földi[14] noted the thermal instability of allyl esters of benzenesulphonic acid which decomposed in an explosive exothermic manner when heated at 180°. Some comparative data on thermal stability of alkyl 2,4-dinitrobenzenesulphonates could be obtained by heating each of the methyl, ethyl, n-propyl, n-butyl, n-amyl and iso-butyl and iso-amyl esters alone under various conditions. Isobutyl and isoamyl 2,4-dinitrobenzenesulphonates decomposed violently after a few minutes at 100°, but the n-propyl, n-butyl and n-amyl esters took longer (some 20–30 min) to reach the critical stage. This sudden exothermic reaction never occurred with the methyl and ethyl esters which evolved gas with progressive rapidity at temperatures up to 210°. After heating at 100° for 1 hr, methyl and ethyl 2,4-dinitrobenzenesulphonates gave, respectively, 5% and 10% of parent acid, most of the ester being recovered unchanged.

The alkyl 2,4-dinitrobenzenesulphonates were heated in dry toluene for different periods of time at various temperatures; the weight of 2,4-dinitrobenzenesulphonic acid produced was taken as a measure of the extent of decomposition. With the esters possessing straight-chain alkyl groups, only traces of the parent acid were formed when each was heated in refluxing toluene for ½ hr. Even with nitrobenzene at temperatures of 100–110°, no more than 4–5% of acid was produced, though as the temperature was increased to 210°, methyl and ethyl esters decomposed smoothly, but the n-propyl, n-butyl and n-amyl esters showed sudden reaction. The corresponding isoalkyl compounds showed considerable decomposition when heated in toluene, the isobutyl more than the isoamyl.

It has been suggested by earlier workers[7,8,11] that the parent acid catalyses the thermal decomposition of esters of aromatic acids. In the alkylation of benzene by means of benzyl benzenesulphonates, Nenitzescu *et al.*[15] added benzenesulphonic acid to initiate the reaction in some cases. We have found that addition of small quantities of 2,4-dinitrobenzenesulphonic acid to each of n-butyl and n-amyl 2,4-dinitrobenzenesulphonate in refluxing toluene resulted in no significant increase in decomposition.

Previous studies of thermal decomposition have shown that methyl is more stable than ethyl benzenesulphonate.[8] Methyl and ethyl 2,4-dinitrobenzenesulphonate show little difference in their stability, but the n-propyl, n-butyl and n-amyl esters are much less stable than these first two members of the series. Lunt[3] mentions thermal

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[15] V. Ioan, C. D. Nenitzescu and co-workers, *Bull. Soc. chim. Fr.* 1272, 1279 (1955); *Acad. R.P.R. Studii si Cercetari de Chim.* **4**, 207 (1956); **7**, 345, 355 (1959); *Acta. chim. Acad. Sci. Hung.* **12**, 195 (1957); *Chem. Ber.* **90**, 585 (1957); *Tetrahedron* **19**, 323, 335 (1963).

instability of the esters of 2,4-dinitrobenzenesulphonic acid, especially above 140°. Our main use for such esters is in quaternization reactions and stable, unreactive bases require heating in a melt without solvent. The poor thermal stability of the isoesters therefore limits their scope for such reactions; we intend to report shortly on their suitability for the quaternization of weak bases like 1,2,3- and 2,1,3-benzothiadiazole.

Földi[10] first reported that the benzyl group could be introduced into aromatic systems by thermal decomposition of benzyl benzenesulphonate in an excess of an aromatic solvent; such behaviour has been the subject of kinetic studies.[15,16] Hickinbottom *et al.*[11] have greatly enlarged the scope of thermal alkylation reactions. These authors found that while there was some evidence for a reaction path involving bimolecular displacement, they were in favour of a carbonium-ion mechanism. Thus the course of thermal alkylation may be represented as follows:

$$\mathrm{Alk{\cdot}O{\cdot}SO_2R} \longrightarrow \mathrm{Olefin} + \mathrm{RSO_2{\cdot}OH} \qquad \text{(i)}$$

$$\mathrm{Alk{\cdot}O{\cdot}SO_2R} \xrightarrow{\mathrm{RSO_2OH}} \left[\begin{matrix}\mathrm{Alk{\cdot}O{\cdot}SO_2R}\\ \mathrm{H}\end{matrix}\right]^{+} \longrightarrow \mathrm{Alk^{+}} + \mathrm{RSO_2{\cdot}OH} \qquad \text{(ii)}$$

$$\mathrm{Alk^{+}} + \mathrm{ArH} \longrightarrow \mathrm{AlkAr} + \mathrm{H^{+}} \qquad \text{(iii)}$$

The initial phase in the absence of acid is thermal decomposition to olefin and free sulphonic acid, followed by proton-catalysed decomposition of the ester to sulphonic acid and carbonium ion. At stage (ii) the carbonium ion $\mathrm{Alk^+}$ may, by loss of a proton to $\mathrm{R\,SO_3^-}$ give more olefin (or polymerize) if stage (iii) is slow because of deactivation of the aromatic nucleus.

Pyrolytic eliminations in the absence of solvent (or in an inert solvent) have been studied for a variety of compounds and the most significant mechanism involves a cyclic transition state (an E_i mechanism).[17] Various workers[18–20] have proposed that carboxylic esters undergo thermal decomposition by a homogeneous unimolecular reaction involving a cyclic transition state of the type proposed for the Chugaev reaction.[21]

It seems unlikely that such theories can be applied to alkyl esters of aromatic sulphonic acids since thermal decomposition would never result in alkylation of organic compounds.

Further, sulphonate esters are known to be good reagents for quaternization reactions, whereas carboxylate esters are not; as this is an electrophilic substitution by the ester it indicates a readiness to undergo heterolytic fission. Thus, from the principles established regarding alkylation reactions, it is most probable that in the thermal decomposition of alkyl 2,4-dinitrobenzenesulphonates, a carbonium ion is formed which eliminates a proton, so generating the olefin. This, of course, cannot apply in the case of methyl ester.

Either the relative stability of the esters depends on ease of thermal fission of the alkyl oxygen bond or on stability of the carbonium ion formed. Neither explains why lower alkyl esters of 2,4-dinitrobenzenesulphonic acid are more stable than the higher

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ones, nor why those esters possessing straight-chain alkyl groups are more stable than the corresponding isoalkyl ones. There is a decrease in their effectiveness in quaternization reactions as the series of n-alkyl 2,4-dinitrobenzenesulphonates is ascended[22] (a possible indication that readiness to undergo heterolytic fission decreases, though it may be due to decreased electrophilic character of the positive species) and such evidence as is available on the stability of carbonium ions leads one to believe that chain branching increases stability. However, the violent decompositions reported may be dependent upon the effectiveness of proton catalysis by the free acid formed in the course of the reaction.

As has been found in quaternization experiments, the esters of sulphonic acids differ greatly from those of carboxylic acids. Furthermore the hydrolysis of the latter in water is, in general, very slow, whereas the former react fairly readily. In studies of the thermal stability of alkyl 2,4-dinitrobenzenesulphonates it is important to employ freshly-prepared materials, as the esters decompose during storage, presumably due to hydrolysis. In some thermal alkylations the initial production of parent acid may be by hydrolysis rather than by thermal decomposition. Földi[8] reported that alkyl and benzyl benzenesulphonate decompose upon standing at room temperature, the acid, (which is deliquescent) formed accelerating the change. Hickinbottom and Rogers[23] found the same with certain esters of toluene-*p*-sulphonic acid. Mallion and Mann[24] reported the observation of Professor Holliman that methyl 2,4-dinitrobenzenesulphonate is rapidly hydrolysed by damp air to the free sulphonic acid. Studies on the hydrolysis of alkyl 2,4-dinitrobenzenesulphonates are in progress and will be reported later.

EXPERIMENTAL

General methods for the preparation of the alkyl 2,4-*dinitrobenzenesulphonates*. Commercial 2,4-dinitrobenzenesulphonyl chloride (M & B. laboratories) was purified by recrystallization from benzene–pet. ether (b.p. 60–80°); pale-yellow crystals were obtained of m.p. 102°. (Lunt[3] gives m.p. 102° from light petroleum (b.p. 60–80°) Willgerodt and Mohr[25] m.p. 101–102°). The alcohols were thoroughly dried[26] before use and magnesium alkoxides were prepared according to the method of Hickinbottom.[27]

Alkoxide method

The procedure of Chadbourne and Nunn[13] was used to obtain crude samples of methyl and ethyl 2,4-dinitrobenzenesulphonates by interaction of 2,4-dinitrobenzenesulphonyl chloride in dry toluene with the requisite sodium alkoxide. The pale-yellow solid was dissolved in dry chloroform and the solution filtered to remove insoluble matter—a varying quantity of a yellow-brown, water-soluble solid. Evaporation to dryness gave a white material sufficiently pure for use in quaternization experiments. Further purification could be effected by recrystallization from chloroform instead of toluene–pet. ether (b.p. 60–80°). Pure methyl ester was obtained as white needles of m.p. 83–84°. (Chadbourne and Nunn[13] 84–85°, Kiprianov and Tolmachev[12] 86·5°, Lunt[3] 82–83°). Pure ethyl ester was obtained as white needles of m.p. 101–102° (Chadbourne and Nunn[13] 101–102°, Kiprianov and Tolmachev[12] 97°, Lunt[3] 97°). Similarly, n-propyl ester was obtained as white needles (from $CHCl_3$) m.p. 106–107° (Chadbourne and Nunn[13] 106–107°).

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TABLE 1. RESULTS OF 0·04 MOLE SCALE EXPERIMENTS

Ester	Crude product		Product after treatment with chloroform		% Yields†			
	Wt. (g)	m.p.	Wt. (g)	m.p.	R & N	C & N	K & T	LUNT
	6·45	72–75°	3·60	80–82°	34			
	8·45	75–80°	6·25	80–82°	60			
Methyl	7·35	79–81°	6·15	80–82°	59	82	50*	57
	3·85	78–80°	3·45	80–82°	33			
	7·75	75–80°	6·15	80–82°	59			
	7·65	98–100°	5·25	100–101°	48			
	5·60	96–98°	3·75	100–101°	34			
Ethyl	7·75	95–98°	5·85	100–101°	53	84	42*	73
	6·45	97–99°	4·15	100–101°	38			
	8·90	98–100°	8·25	100–101°	75			
n-Propyl	6·50	103–105°	5·80	105–106°	50	86		

Yields are as quoted by the various authors......
† R & N—Ralph and Nunn (present paper)
C & N—Chadbourne and Nunn[18]
K & T—Kiprianov and Tolmachev[12]
LUNT—Lunt[3]
* Results of 0·02 mole scale experiments.

Attempts to increase the scale of the reaction led to serious decreases in the yield as Chadbourne[28] had found.

Lutidine method

The removal of HCl between 2,4-dinitrobenzenesulphonyl chloride and the alcohol, by means of dry 2,6-lutidine, was carried out according to the method of Chadbourne and Nunn[18] who used a hundred-fold excess of the alcohol to obtain material free from unchanged chloride.

The crude products were suitable for quaternization reactions. Lower members of the series of n-alkyl 2,4-dinitrobenzenesulphonates may be purified by recrystallization from dry $CHCl_3$. This is unsuitable for higher members (increasing solubility as the series is ascended), where toluene–pet. ether (60–80°) may be used. Heating of the isoalkyl 2,4-dinitrobenzenesulphonates should be avoided, so purification is effected by dissolution in cold toluene and reprecipitation with pet. ether (60–80°).

Thermal decomposition of the alkyl 2,4-dinitrobenzenesulphonates. The esters were freshly prepared and carefully purified before use.

Heating alone

The ester (1·0 g) was melted and then heated in a boiling water-bath for a period of time not exceeding 1 hr. The extent of decomposition of methyl and ethyl 2,4-dinitrobenzenesulphonates was determined by treating the brown-black syrup with toluene (20–25 ml), and collecting the insoluble material, which was then washed with a little $CHCl_3$ (to remove unchanged ester). Addition of pet. ether (60–80°) to the toluene filtrate enabled unchanged ester to be reclaimed. All the other alkyl 2,4-dinitrobenzenesulphonate assumed a brown turbidity and then suddenly underwent an exothermic reaction leaving a black residue.

Willgerodt and Mohr[25] 106–108°. Elgersma[29] 108°. Chadbourne[28] 106–107°. When heated to 210° (boiling nitrobenzene) the methyl and ethyl 2,4-dinitrobenzenesulphonates evolved gas vigorously leaving a black tar, but no explosion occurred.

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[29] J. N. Elgersma, *Rec. Trav. Chim.* **48**, 752 (1929).

TABLE 2

Ester	Nature of alcohol	Crude product		Scale of reaction	% Yields†			m.p. of Pure compound		
		Yield(g)	m.p.		R & N	C & N	LUNT	R & N	C & N	LUNT
Ethyl*	Dry	5·85 5·75	99–100°	0·04 mole	53 52			101–102°		
n-Propyl	Dry	4·81	105–106°	0·02 mole		83			106–107°	
	Dry	21·70	104–106°	0·10 mole	75			106–107°		
n-Butyl	Dry	3·1	66–67°	0·02 mole			51			68°
	Dry	4·10	68–69°	0·02 mole		67·5			68–69°	
	Dry	18·80	66–68°	0·10 mole	62			68–69°		
	Undried	17·70			58					
Isobutyl	Dry									74–75°
	Dry	4·41	84–85°	0·02 mole		73			85–86°	
	Dry	20·50	83–85°	0·10 mole	67			85–86°†		
	Undried	19·45			64					
n-Amyl	Undried	19·75	73–75°	0·10 mole	62			75–76°		
Isoamyl	Undried	19·35	65–67°	0·10 mole	61			66–68°§		

n-*Amyl 2,4-dinitrobenzenesulphonate* (Found: C, 41·7; H, 4·5; H, 8·9; S, 9·8. $C_{11}H_{14}N_2O_7S$ requires: C, 41·5; H, 4·4; N, 8·8; S, 10·1%.) →

Isoamyl 2,4-dinitrobenzenesulphonate. (Found: C, 40·6; H, 4·2; N, 8·9; S, 10·0. $C_{11}H_{14}N_2O_7S$ requires: C, 41·5; H, 4·4; N, 8·8; S, 10·1%.)

Yields are as quoted by the various authors.....

† R & N—Ralph and Nunn (present paper)
C & N—Chadbourne and Nunn[18]
K & T—Kiprianov and Tomachev[12]
LUNT—Lunt[1]

* With the ethyl ester, it is vital that the temp of the reaction mixture be kept at 0° (or below); quaternization of 2,6-lutidine occurs readily at room temp but is only slight at 0°.

‡ Partially melts at 74–75° but a clear liquid is not formed until temp reaches 85–86°; darkens on further heating.

§ Does not melt sharply and darkens on further heating.

TABLE 3

Ester	Period of heating	Temp of decomp.	Decomposition product	Unchanged ester	comments
Methyl	1 hr	Very slight elevation over 100°	0·05 g m.p. 104–106°†	0.90 g m.p. 79–81°	
Ethyl	1 hr	Slight elevation over 100°	0·10 g m.p. 104–106°†	0·80 g m.p. 99–101°	
n-Propyl	15–20 min	over 200°	Carbon-black residue		violent reaction
n-Butyl	20–25 min	over 200°	Carbon-black residue		reaction violent
n-Amyl	30 min	~120°	Black tar		brisk reaction
Isobutyl	5 min	over 200°	Carbon-black residue		violent reaction
Isoamyl	5 min	~125°	Black tar		rapid reaction

† Lit. m.p. for trihydrate of 2,4-dinitrobenzenesulphonic acid. Willgerodt and Mohr[25] 106–108°. Elgersma[29] 108°. Chadbourne[28] 106–107°.

Heating in a solvent

(a) *Toluene.* The ester (1·0 g) was heated in dry toluene as specified in Table 4. The reaction mixture was then cooled and any deposited solid collected, washed with a small volume of $CHCl_3$ and dried. The white to grey material obtained usually had m.p. in the range 103–106°, indicating that it was 2,4-dinitrobenzenesulphonic acid; this was confirmed by the intense yellow-brown colour of an alkaline solution (due to production of 2,4-dinitrophenol).[26] Unchanged ester was reclaimed by addition of pet. ether (60–80°) to the toluene filtrate.

TABLE 4

Ester	Vol. of toluene†	Temp.*	Period of heating*	Amount of 2,4-D.N.B.S.A.	Wt. of reclaimed ester (g)
Methyl	25 ml	110°	½ hr slight darkening	trace	0·925
Ethyl	20 ml	110°	½ hr slight darkening	trace	0·95
n-Propyl	15 ml	110°	½ hr slight darkening	trace	0·925
n-Butyl	10 ml	110°	½ hr no darkening	none	0·95
n-Amyl	10 ml	110°	½ hr no darkening	none	0·925
Isobutyl	10 ml	110°	¼ hr much	0·45 g	0·30
			½ hr darkening	0·85 g	none
		100°	½ hr considerable	0·05 g	0·80
			1 hr darkening	0·25 g	0·50
		80°	6 hr slight darkening	0·10 g	0·75
Isiamyl	10 ml	110°	½ hr considerable	0·10 g	0·70
			1 hr darkening	0·20 g	0·60
		100°	1 hr slight darkening	0·05 g	0·80

† Volume of toluene used is related to solubility of the ester.

* Temp and period of heating are related to conditions used for the quaternization of weak heterocyclic bases.

Both n-butyl and n-amyl 2,4-dinitrobenzenesulphonates (1·0 g of each ester), heated in dry toluene (10 ml) for ½ hr at 110° with a small amount of 2,4-dinitrobenzenesulphic acid added (0·05 g) each produced as a result only 0·075 g of the acid.

(b) *Nitrobenzene.* A polar solvent was used, in place of toluene, to see if this would increase decomposition of the n-alkyl 2,4-dinitrobenzenesulphonates. Each of the esters (1·0 g) heated for 1 hr at 100° in dry nitrobenzene (10 ml) gave 0·05 g of parent acid when the reaction was treated with toluene. In refluxing nitrobenzene (~210°), the methyl and ethyl esters slowly darkened and evolved gas briskly, but higher members showed sudden reaction. As a typical example, n-butyl 2,4-dinitrobenzenesulphonate, heated at 210° for a few seconds, darkened rapidly; the reaction mixture, quickly cooled and treated with toluene, gave 0·65 g of acid, demonstrating serious decomposition.

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