SYNTHESIS AND THERMOCHEMICAL PROPERTIES OF DIALKYLFUROXANS

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A systematic study of the thermochemistry of dialkylfuroxans has not been made up to now. Only one communication exists in the literature on a study of the thermochemical characteristics of dimethylfuroxan [1]. The principal reason for the absence of information on the properties of the dialkylfuroxans is the complexity of obtaining highly pure products when using the known methods for their preparation.

The most convenient method for the synthesis of the dialkylfuroxans is based on the reaction of glyoximes, which are obtained from the corresponding diketones, with nitrogen tetroxide [2,3]. Still another method for the preparation of the dialkylfuroxans is based on the reaction of dialkyldinitroethylenes $R-C(NO_2)=C(NO_2)-R$ with sodium azide [4,5]. Both the diketones and the dialkyldinitroethylenes are obtained mainly as difficultly separable mixtures during the nitration of dialkylacetylenes. The separation of the reaction products and their purification are complicated and hazardous. This is responsible for the unsuitability of the described methods for the preparation of substantial amounts of the dialkylfuroxans.

The most promising method for the preparation of the dialkylfuroxans is based on the nitrosation of ketones, for example, with alkyl nitrites [6]:

$$R-\underset{\underset{O}{\|}}{C}-CH_2-R' \xrightarrow{R''ONO} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-R'$$

Then the isonitroso ketones are reacted with hydroxylamine in methanol medium and the obtained dialkylglyoximes $R-\underset{\underset{NOH}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-R'$ are converted to the dialkylfuroxans by reaction with nitrogen tetroxide. This method was adopted in the present paper to synthesize the dialkylfuroxans. As models for the study we took ketones with the general formula $R-\underset{\underset{O}{\|}}{C}-CH_2-R'$. The constants of the synthesized dialkylfuroxans are given in Table 1. The structure of the obtained compounds was confirmed by IR spectroscopy. A distinctive feature of the proposed method is the good yield of the products at each step, and also their high degree of purity.

For compounds (I)-(III) and (VI) we experimentally measured the heats of combustion (ΔH^0_{comb}) and calculated the enthalpies (ΔH^0_f) of formation (Table 2). The found combustion heats are in good agreement with the calculated values, which were obtained by adding the corresponding number of terms per CH_2 group to $H^0_{comb} = -592.0$ kcal/M for dimethylfuroxan [1]. The contribution per CH_2 group was taken equal to −156.3 kcal/M for the straight-chain alkanes. As a result, it was possible to reliably calculate the heats of combustion and the enthalpies of formation for any of the dialkylfuroxans.

EXPERIMENTAL METHOD

Synthesis of Isonitroso Ketones (General method). The ketone taken for nitrosation was placed in a Drexel flask, a small amount of HCl was added, and either ethyl nitrite or methyl nitrite was bubbled in on the basis of 1.1 M of nitrite per mole of ketone. The reaction mixture was kept at 30-40° for 6 h, neutralized with aqueous ammonia solution, and filtered. The filtrate was washed with water, dried over $MgSO_4$ and vacuum-distilled. The constants of the obtained isonitroso ketones are given in Table 3.

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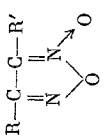
TABLE 1. Constants of Dialkylfuroxans



Compound	R	R′	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}, g/cm³	n_D^{20}	Found, % C	Found, % H	Found, % N	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % N
(I)	C_2H_5	C_3H_7	82	86—87 (1)	1,0678	1,4768	53,04	7,69	17,81	$C_7H_{12}N_2O_2$	53,82	7,67	17,95
(II)	C_2H_7	C_4H_9	93	110—111 (1)	1,0264	1,4751	58,11	8,33	15,00	$C_8H_{14}N_2O_2$	58,69	8,69	15,22
(III)	CH_3	C_3H_7	87	82—83 (1)	1,1071	1,4782	49,80	6,95	19,45	$C_6H_{10}N_2O_2$	50,70	7,04	19,72
(IV)	CH_3	C_4H_9	92	100—101 (1)	1,0794	1,4772	53,69	7,60	17,76	$C_7H_{12}N_2O_2$	53,82	7,67	17,95
(V)	CH_3	C_5H_{11}	90	108—109 (1)	1,0525	1,4756	56,22	8,13	16,35	$C_8H_{14}N_2O_2$	56,47	8,24	16,47
(VI)	CH_3	C_6H_{13}	86	114—115 (1)	1,0274	1,4751	58,44	8,51	15,37	$C_9H_{16}N_2O_2$	58,69	8,69	15,22
(VII)	CH_3	C_7H_{15}	90	132—133 (3)	1,0141	1,4724	60,52	9,11	14,28	$C_{10}H_{18}N_2O_2$	60,60	9,09	14,14

TABLE 2. Thermochemical Characteristics of Dialkylfuroxans

Compound	ΔH^0_{comb}, kcal/M experiment	ΔH^0_{comb}, kcal/M calculated	ΔH^0_f, kcal/M
(I) $C_2H_5C_2N_2O_2C_3H_7$ (*l*)	1060,8±0,6	1060,9	—7,5±0,6
(II) $C_3H_7C_2N_2O_2C_4H_9$ (*l*)	1374,3±0,6	1373,5	—18,7±0,6
(III) $CH_3C_2N_2O_2C_3H_7$ (*l*)	904,8±0,6	904,6	—1,1±0,6
(IV) $CH_3C_2N_2O_2C_4H_9$ (*l*)		1060,9	—7,4 *
(V) $CH_3C_2N_2O_2C_5H_{11}$ (*l*)		1217,2	—13,4 *
(VI) $CH_3C_2N_2O_2C_6H_{13}$ (*l*)	1373,7±0,7	1373,5	—19,7±0,7
(VII) $CH_3C_2N_2O_2C_7H_{15}$ (*l*)		1529,8	—25,6 *

*Calculated values.

Synthesis of Dialkylglyoximes (General method). Hydroxylamine hydrochloride (1.1 M) was dissolved in methanol and conc. KOH (1.1 M) solution was added. The KCl precipitate was filtered rapidly, and 1 M of the isonitroso ketone was added to the filtrate. The reaction mixture was kept at 30° for 7 h, and then it was cooled to –10°. The obtained crystals of the glyoxime were filtered, dried in vacuo, and recrystallized from aqueous ethanol. The melting points of the obtained glyoximes are given in Table 4.

Synthesis of Dialkylfuroxans. We will discuss the preparation of the dialkylfuroxans on the example of propylbutylfuroxan (II). Compounds (I) and (III)-(VII) were obtained in a similar manner.

With vigorous stirring, to a suspension of 75 g of propylbutylglyoxime in 600 ml of $CHCl_3$ at 0° was added 25.6 ml of nitrogen tetroxide. The mixture was stirred at 0° for 6 h, poured into 500 ml of water, washed with 3% urea solution (3 × 200 ml), then with water, and dried over $MgSO_4$. After removal of the solvent the residue was vacuum-distilled. We obtained 69 g (93%) of propylbutylfuroxan.

Thermochemical Experiment. The combustion heats of the dialkylfuroxans were determined in the calorimetric setup described in [7], with a heat value of 350.43 ± 0.11 cal/deg, which was determined by the combustion of standard benzoic acid with a combustion heat of 6318.1 cal/g. The compound was placed in a platinum crucible and ignited by a pulse current using a copper wire that was immersed in the liquid sample. The dialkylfuroxans burn poorly under normal conditions (the O_2 pressure in the

TABLE 3. Isonitroso Ketone Constants R—C(=O)—C(=NOH)—R′

R	R′	Bp, °C (p, mm of Hg)	Mp, °C	n_D^{20}
C_2H_5	C_3H_7	80—81 (3)	—	1,4608
C_2H_7	C_4H_9	98—99 (1)	—	1,4624
CH_3	C_3H_7	73—74 (1)	45,5—46	—
CH_3	C_4H_9	86—87 (1)	57—58	—
CH_3	C_5H_{11}	104—105 (2)	—	1,4502
CH_3	C_6H_{13}	124—125 (2)	—	—
CH_3	C_7H_{15}		51—52	

TABLE 4. Heats of Combustion of Dialkylfuroxans

m, g	m_b, g	ΔT,°	q_{wire}, cal	q_{HNO_3}, cal	q_{wire}, cal	$\Delta u_c'$, cal/g
			Ethylpropylfuroxan (I)			
0,10011	0,03942	2,689	941,95	2,35	10,90	6788,9
0,09938	0,03982	2,678	938,45	2,07	10,29	6786,5
0,10216	0,03901	2,720	953,17	2,26	10,93	6788,5
0,10016	0,04017	2,709	949,31	2,49	12,13	6798,0
0,10133	0,04013	2,725	954,92	2,62	10,36	6793,6
			Propylbutylfuroxan (II)			
0,09860	0,03671	2,795	979,28	2,21	9,73	7458,2
0,09992	0,03661	2,823	989,26	1,93	10,78	7458,7
0,10038	0,03762	2,851	999,07	2,21	9,25	7450,9
0,09950	0,03779	2,835	993,47	2,62	10,40	7454,2
0,10026	0,03913	2,876	1007,84	2,21	10,44	7460,5
			Methylpropylfuroxan (III)			
0,09187	0,06282	2,838	994,52	1,93	10,69	6367,7
0,09661	0,05053	2,700	946,16	2,07	10,03	6363,8
0,10023	0,04988	2,762	967,89	2,35	11,42	6375,0
0,10124	0,05077	2,793	978,75	2,65	11,18	6362,9
0,10146	0,05059	2,791	978,05	2,62	10,42	6360,9
			Methylhexylfuroxan (VI)			
0,10226	0,02592	2,679	938,80	2,62	10,66	7449,3
0,10637	0,02628	2,776	972,79	2,07	11,23	7459,3
0,10049	0,02592	2,640	925,13	2,35	10,77	7446,0
0,10628	0,02594	2,762	967,89	2,62	9,79	7448,2
0,10103	0,02664	2,665	933,89	2,21	10,45	7452,5

TABLE 5. Melting Points of Dialkylglyoximes R—C(NOH)—C(NOH)—R′

R	R′	Mp., °C
C_2H_5	C_3H_7	167—168
C_2H_7	C_4H_9	171—172
CH_3	C_3H_7	172—173
CH_3	C_4H_9	170—171
CH_3	C_5H_{11}	169—169,5
CH_3	C_6H_{13}	168—169
CH_3	C_7H_{15}	164—165

bomb was 30 atm), for which reason standard benzoic acid was used as an auxiliary substance to assure their complete combustion.

The experimentally determined combustion heats of compounds (I)-(III) and (VI) are given in Table 4, where the following designations were adopted: m is the weight of the substance, m_b is the weight of benzoic acid, ΔT is the temperature rise in the experiment taking into account the correction for the heat exchange Q_{total} is the total amount of heat evolved in the calorimeter, q_{HNO_3} and q_{wire} are the corrections for the formation of nitric acid and the combustion of the copper wire, and u_c' is the combustion heat of the compound under the conditions of the calorimetric bomb.

In calculating the standard heats of combustion we inserted the Washburn calorimetric corrections and ΔnRT. The heats of combustion refer to the following reactions:

(I) $C_7H_{12}N_2O_2$ (*l*) + $9O_2$ (g) → $7CO_2$ + $6H_2O$ (*l*) + N_2

(II), (VI) $C_9H_{16}N_2O_2$ (*l*) + $12O_2$ → $9CO_2$ + $8H_2O$ (*l*) + N_2

(III) $C_6H_{10}N_2O_2$ (*l*) + $7{,}5O_2$ → $6CO_2$ + $5H_2O$ (*l*) + N_2

In calculating the enthalpies of formation of the dialkylfuroxans the enthalpies of the formation of CO_2 (g) and H_2O (*l*) were respectively taken equal to –94.051 and –68.317 kcal/M.

CONCLUSIONS

A number of dialkylfuroxans was synthesized and their thermochemical properties, namely the heats of combustion and the enthalpies of formation, were studied.

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