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DETERMINATION OF THE ENTHALPY OF THE 1, 3-DIPOLAR CYCLOADDITION REACTION OF NITRONE ETHERS

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The enthalpy of the 1, 3-dipolar cycloaddition of 2-nitroisoxazoline N-oxide to ethylene has been determined.

In recent years, the attention of chemists has been attracted increasingly to multicenter processes taking place with the cyclic coordinated transfer of electrons. The 1, 3-dipolar cycloaddition reaction discovered at the beginning of the sixties by Huisgen [1] is rapidly assuming the leading role in this type of reaction. Important in the study of 1, 3-dipolar cycloaddition is the elucidation of the general laws of the reaction and the determination of its position in relation to other multicenter processes. The present work, in particular, took as its object the determination of the enthalpy of the reaction. As a concrete example of the reaction, we selected the 1, 3-dipolar cycloaddition of 2-nitroisoxazoline N-oxide to ethylene [2].

Heat of Combustion of 8-Nitroisoxazolizidine*

m	δ	Δt	q'	q''	Q_v
0.19645	0.031	2.391	3.4	7.2	4461.7
0.22519	0.040	2.739	4.0	6.7	4465.1
0.23077	0.041	2.815	4.1	10.6	4462.0
0.23232	0.042	2.833	4.1	9.1	4467.1
0.20484	0.036	2.506	3.8	10.4	4469.3
0.20213	0.036	2.463	3.8	8.8	4458.4

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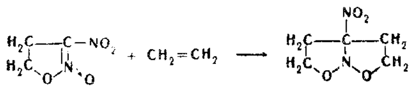
*Q_V = 4463.9±3.2 cal/g; Q_V = 714.8± ±0.5 kcal/mole, ΔH^0 = -29.9±0.5 kcal/mole.



In order to determine the heat effect of this reaction the enthalpy of formation of 8-nitroisoxazolizidine was determined from the heat of combustion of this substance found experimentally (the heat of formation of 2-nitroisoxazoline N-oxide has been determined previously, being −12.2 ± 0.5 kcal/mole [3]).

The compound was burned using the semimicrocalorimetric method in a calorimeter with an energy equivalent of 371.0 cal/deg [4] (1 cal = 4.1840 J). The temperatures were read on a calorimetric thermometer, 1° of which corresponds to 0.666° C. The combustion was performed on repeatedly recrystallized samples obtained by two syntheses.

The results of the combustion of 8-nitroisoxazolizidine given in the table, where m is the weight of the sample in g; δ is the correction for heat exchange with the calorimeter with an isothermal jacket, deg; Δt is the rise in temperature corrected for heat exchange, deg; q' is the heat correction for the formation of nitric acid, cal; q" is the correction for the combustion of the heating wire, cal; Q_V is the heat of combustion of the compound under the bomb conditions, cal/g and kcal/mole; and ΔH^0 is the standard enthalpy of formation of the substance, kcal/mole, calculated with the use of calorimetric corrections (Washburn, et al.) taking into account the heat of formation of the combustion products CO_2 and H_2O, equal to −94.052 and −68.317 kcal/mole, respectively [5].

The heat of formation of 8-nitroisoxazolizidine was found to be −29.9 ± 0.5 kcal/mole.

From the results obtained it is possible to calculate the enthalpy of the 1, 3-dipolar cycloaddition of 2-nitroisoxazoline N-oxide to ethylene, using the enthalpies of formation of 2-nitroisoxazoline N-oxide (−12.2 kcal/mole) and of ethylene (+12.5 kcal/mole). The enthalpy of the reaction is +30.2 ± 1.0 kcal.

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DETECTION OF 5-AMINOPYRIMIDINES

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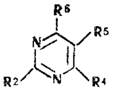
Bindone is conveniently used for the selective detection of 5-aminopyrimidines. Amino groups in positions 2, 4, and 6 of the pyrimidine ring are not detected by this reaction. 5-Acylaminopyrimidines do not react either.

Anhydrobisindandione (bindone) was long ago recognized as a good reagent for primary aromatic and aliphatic amines [1, 2]. There is also information on the possibility of using bindone for detecting some heterocyclic primary amines [1]. There is no information in the literature on the selective detection of amino groups in aminopyrimidines. We propose to use bindone for the selective detection of the 5-amino group in pyrimidine derivatives in the presence of other substituents, including amino groups in other positions. This presents considerable interest, particularly in the production of 5-aminopyrimidines by the reduction of 5-nitro- or 5-nitrosopyrimidines and also in the acylation of 5-aminopyrimidines.

Reactions with Bindone of Compounds of the General Formula



Compound	R^2	R^4	R^5	R^6	Result
I	NH_2	NH_2	NH_2	OH	+
II	OH	NH_2	NH_2	OH	+
III	SH	NH_2	NH_2	OH	+
IV	NH_2	NH_2	$NHCOC_6H_5$	OH	–
V	NH_2	NH_2	$NHCOCH_2Cl$	OH	–
VI	NH_2	NH_2	$NHCOCH_3$	OH	–
VII	CH_3	NH_2	H	CH_3	–
VIII	NH_2	NH_2	H	OH	–
IX	SH	NH_2	H	OH	–
X	SH	NH_2	H	H	–
XI	OH	NH_2	H	OH	–
XII	SH	NH_2	NO	OH	–
XIII	NH_2	NH_2	NO	OH	–
XIV	Cl	NH_2	NO_2	CH_3	–
XV	OH	NH_2	NO_2	CH_3	–
XVI	H	NH_2	NH_2	NH_2	+
XVII	NH_2	H	NH_2	H	+*

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* In this case, the reaction takes place without heating. Even under these conditions, the blue-violet color rapidly changes into dark brown.

The reaction was carried out in the usual way [2], i.e., by boiling a small amount of the substance under investigation with bindone in glacial acetic acid for several minutes. Ordinary 98% acetic acid may give negative results even when an amine is present. Amino groups in positions 2, 4, and 6 of the pyrimidine ring and 5-acylaminopyrimidines, adenine, and guanine are not detected. Pyrimidines having amino groups in position 5 give an intense blue-violet or violet color (at low concentrations a violet-red color) even on brief heating, and when such an amino group is absent they give a yellow, red-brown, or brown color. The reaction has been carried out with a series of aminopyrimidines (see table).

The sensitivity of the reaction was determined for some compounds. Compound III is detected at a concentration of not lower than 0.0003 M and compounds XVI and XVII at 0.003 M.

The reaction can be used conveniently for following the starting materials and reaction products in certain syntheses for pyrimidines and purines.

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