THE ENERGY OF THE N → O BOND IN 3-NITROISOXAZOLINE N-OXIDE

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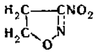
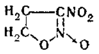
The enthalpy of combustion of 3-nitroisoxazoline has been determined as $\Delta H_C^{298.15} = -414 \pm 0.3$ kcal/mole and that of 3-nitroisoxazoline N-oxide as $\Delta H_C^{298.15} = -406.6 \pm 0.5$ kcal/mole. From the values for the heats of combustion and evaporation, the standard enthalpies of formation have been calculated and the energy of the N → O bond has been evaluated at 64 ± 3 kcal/mole.

The preparation of 3-nitroisoxazoline (I) and of 3-nitroisoxazoline N-oxide (II) has been described previously [1, 2].

These compounds have been patented as physiologically active substances [3], and are interesting from the structural point of view because they permit an evaluation of the dissociation energy of the N → O bond, information on the strength of which is lacking.





The calculation of the dissociation energy of the bond, D(N → O), was carried out from the formula:

$$D(\mathrm{N}\to\mathrm{O}) = \Delta H_f^{298.15}\mathrm{I}\,(g) + \Delta H_f^{298.15}\mathrm{O}\,(g) - \Delta H_f^{298.15}\mathrm{II}\,(g),$$

where $\Delta H_f^{298.15}$ I (g) is the enthalpy of formation of 3-nitroisoxazoline in the gaseous phase, $\Delta H_f^{298.15}$ O (g) is the enthalpy of formation of atomic oxygen, 59.54 kcal/g-at, and $\Delta H_f^{298.15}$ O II (g) is the enthalpy of formation of 3-nitroisoxazoline N-oxide in the gaseous phase.

The heat of evaporation of I required for the calculation was obtained from the variation of the saturated vapor pressure as a function of the temperature measured by a direct manometric method, $\log p = 8.89 - 3.09/T$. From this equation the heat of evaporation was calculated as 14.1 ± 0.2 kcal/mole and the enthalpy of formation of I in the gaseous phase as 9.3 ± 0.5 kcal/mole.

On being heated, substance II decomposes with the liberation of oxygen and the formation of I, and, therefore, to evaluate the heat of evaporation of II we used the property of the additivity of the contributions of the individual bonds, atoms, and groups to the heat of evaporation, giving a deviation from the experimental value of 1–2 kcal/mole [5]. The heat of evaporation of pyridine N-oxide was obtained in precisely the same way as that for I; it was 13.0 ± 0.3 kcal/mole which is ~ 3 kcal/mole higher than that of pyridine, 9.7 kcal/mole [6]. On the basis of the additivity principle, the heat of evaporation of II is 3 kcal/mole greater than the heat of evaporation of I and must be about 17 kcal/mole, while the enthalpy of formation of II in the gaseous phase is 5 ± 2 kcal/mole.

On the basis of these results, the dissociation energy of the N → O bond may be evaluated as 64 ± 3 kcal.

EXPERIMENTAL

A sample of I was purified by vacuum distillation and was chromatographically pure: d_4^{20} 1.4022; n_D^{20} 1.5049. A sample of II was purified by repeated recrystallization, mp 96.5° C. The combustion of the substances was carried out in a semimicro calorimeter [4] with a heat of 371.0 ± 0.2 cal/deg determined with standard benzoic acid having a heat of combustion of 6318.1 cal/g.

Table 1 gives the results of experiments on the combustion of substance I. Combustion was carried out in thin-walled glass tubes weighing 30–40 mg. The amounts of substance present could not give the same temperature rise as in the standard calorimetric method (2.5–3 degrees on a calorimetric thermometer for which one degree = 0.666° C, and, therefore, in the combustion of I a polyethylene film with a heat of combustion of 11,110 ± 1.5 kcal/g (from 20 experiments) was used as the auxiliary substance.

Data for the heat of combustion of II is given in Table 2; the substance was burned in the form of tablets.

In the tables: m is the weight of the sample of the substance, g; m' is the weight of the auxiliary substance (polyethylene), g; δ is the correction for the exchange of heat between the calorimeter and the isothermal jacket, degrees; Δt is the rise in temperature corrected for heat exchange, degrees; q is the heat liberated in the combustion of the auxiliary substance, cal; q' is the correction for the formation of nitric acid, cal; q" is the correction for the combustion of the heating

Table 1

Heat of Combustion of 3-Nitroisoxazoline*

m	m'	δ	Δt	q	q'	q''	Δu_B
0.19021	0.02001	0.032	2.479	222.3	2.8	14.6	3575.0
0.26126	0.01764	0.046	3.077	196.0	3.6	6.7	3580.0
0.23932	0.01627	0.040	2.819	180.8	3.4	6.3	3573.8
0.14191	0.05097	0.042	2.920	566.3	2.6	6.9	3576.2
0.13359	0.05001	0.041	2.812	555.6	2.5	7.0	3579.6
0.24420	0.02435	0.048	3.118	270.5	3.6	8.2	3581.1

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*$\Delta u_B = 3577.6 \pm 2.7$ kcal/g; $H_c^{298.15} = -414.0 \pm 0.3$ kcal/mole; $\Delta H_f^{298.15} = -4.8 \pm 0.3$ kcal/mole; see also the explanation in the text.

Table 2

Heat of Combustion of 3-Nitroisoxazoline N-Oxide*

m	δ	Δt	q'	q''	Δu_B
0.28899	0.036	2.437	3.7	9.1	3084.2
0.28970	0.037	2.450	3.7	10.4	3089.1
0.29623	0.039	2.515	4.0	13.5	3090.8
0.29051	0.036	2.464	3.9	10.0	3098.7
0.33870	0.043	2.867	4.2	11.9	3093.0

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*Δu_B = 3091.2 ± 3.7 cal/g; $\Delta H_c^{298.15}$= -4906.6 ± 0.5 kcal/mole; $\Delta H_f^{298.15}$= 12.2 ± 0.5 kcal/mole; see also explanation in the text.

wire, cal; Δu_B is the heat of combustion of the compound under the conditions of the calorimetric bomb, cal/g; $\Delta H_c^{298.15}$ is the enthalpy of the combustion of the substance under standard conditions; and $\Delta H_f^{298.15}$ is the standard enthalpy of formation of the substance taking the enthalpies of formation of the combustion products CO_2 and H_2O as −94.051 and −68.317 kcal/mole, respectively.

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