Thus, the character of the changes in the temperature dependences of RTL intensity in passing from "perfect" glasses to glasses with cracks or to polycrystalline samples can be explained by assuming that RTL in the 140—220 K range is connected with the recombination of the $SO_4^{\cdot -}$ radicals stabilized on the surface of sulfuric acid crystals.

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Dinitramide and its salts

11. Synthesis of dinitramide by nitration of nitramide with nitryl salts

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Nitration of nitramide to dinitramide with nitryl salts is described.

Key words: nitration, nitryl salts, nitramide, dinitramide.

In previous reports,[1—3] we have described "organic" methods of synthesis of some inorganic compounds, *viz.*, dinitramide salts (DNA). In the present paper, DNA was synthesized by methods of inorganic chemistry: the nitration of nitramide (NA). NA is a rather labile compound, which is decomposed to N_2O and H_2O under the action of acids and particularly bases,[4] which rules out the possibility of "alkaline" nitration. The nitration of NA with nitric acid or sulfuric-nitric mixtures is difficult due to the instability of NA and DNA in these media. Also, it is necessary to assume that NA has low nucleophilicity. For the these reasons, our attempts to nitrate NA to DNA with a mixture of HNO_3 with Ac_2O or N_2O_5 were unsuccessful. The treatment of NA with a mixture of HNO_3 and trifluoroacetic anhydride afforded only a trace amount of DNA. However, it appeared that the quantitative transformation of NA to DNA is possible in nitration with nitryl salts.*

$$H_2N{-}NO_2 + NO_2^+X^- \longrightarrow HN(NO_2)_2 + HX$$

$$X = BF_4,\ SO_3F,\ S_2O_7H,\ S_2O_7NO_2$$

A thorough study of this reaction showed that the yield of DNA depends substantially on the type of nitryl salt, solvent used, temperature, and reaction time (Table 1). Nitryl tetrafluoroborate (NTFB), nitryl fluorosulfonate (NFS), nitryl hydrogen pyrosulfate (NHP), and nitryl pyrosulfate (NP) were studied as the salts.

The easiest nitration proceeds for NTFB and NFS. Under their action in MeCN at −20—0 °C, NA transforms to DNA in a quantitative yield after only 5 min. Increasing the reaction time results in a decrease in the yield of DNA. MeCN, CH_2Cl_2, EtOAc, and hexane were studied as solvents. It appeared that for the nitration of NA with NTFB or NFS, the best yields of DNA were achieved in MeCN. When CH_2Cl_2 or EtOAc were used, the yield of DNA decreased by several times, and in hexane, DNA was not formed at all. Apparently, this result may be substantially explained by the different solubility of the starting materials in these solvents. In

* For Part 10, see Ref. 3.
* See also Ref. 5.

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Table 1. Dependence of the yield of DNA on the conditions of the nitration of nitramide

Nitrating agent	Solvent	Reaction temperature/°C	Reaction time/min	Yield of DNA (%)
NO_2BF_4	MeCN	−40	60	94
NO_2BF_4	MeCN	0	5	99
NO_2BF_4	MeCN	0	60	92
NO_2BF_4	MeCN	20	5	64
NO_2BF_4	MeCN	20	30	52
NO_2BF_4	MeCN	20	60	21
NO_2BF_4	MeCN	40	5	11
NO_2BF_4	MeCN	40	30	0
NO_2BF_4	CH_2Cl_2	−20	90	16
NO_2BF_4	CH_2Cl_2	−20	5	2
NO_2SO_3F	MeCN	−40	5	85
NO_2SO_3F	MeCN	−20	5	100
NO_2SO_3F	MeCN	−10	5	95
NO_2SO_3F	MeCN	0	5	91
NO_2SO_3F	EtOAc	−40	20	33
NO_2SO_3F	EtOAc	−20	20	16
NO_2SO_3F	EtOAc	0	20	3
NO_2SO_3F	CH_2Cl_2	−40	90	17
NO_2SO_3F	CH_2Cl_2	−20	5	34
NO_2SO_3F	CH_2Cl_2	−20	45	64
NO_2SO_3F	CH_2Cl_2	−20	90	57
NO_2SO_3F	CH_2Cl_2	0	5	51
NO_2SO_3F	CH_2Cl_2	0	45	Traces
$NO_2S_2O_7H$	CH_2Cl_2	−40	100	15
$NO_2S_2O_7H$	CH_2Cl_2	−20	5	23
$NO_2S_2O_7H$	CH_2Cl_2	−20	100	17
$NO_2S_2O_7H$	CH_2Cl_2	0	5	27
$NO_2S_2O_7H$	CH_2Cl_2	0	20	16
$NO_2S_2O_7H$	CH_2Cl_2	0	100	2
$NO_2S_2O_7H$	CH_2Cl_2	10	5	23
$(NO_2)_2S_2O_7$	CH_2Cl_2	−40	5	12
$(NO_2)_2S_2O_7$	CH_2Cl_2	−40	90	49
$(NO_2)_2S_2O_7$	CH_2Cl_2	−40	120	43
$(NO_2)_2S_2O_7$	CH_2Cl_2	−20	5	27
$(NO_2)_2S_2O_7$	CH_2Cl_2	−20	30	36
$(NO_2)_2S_2O_7$	CH_2Cl_2	−20	90	44
$(NO_2)_2S_2O_7$	CH_2Cl_2	−20	120	43
$(NO_2)_2S_2O_7$	CH_2Cl_2	0	5	36
$(NO_2)_2S_2O_7$	CH_2Cl_2	0	90	3

fact, NA is very soluble in MeCN, slightly soluble in CH_2Cl_2, and practically insoluble in hexane. NTFB is substantially soluble only in MeCN. One can assume that the nitration of NA in MeCN proceeds in a homogeneous medium.

The temperature and the reaction time significantly affect the yield of DNA. The maximum yields of DNA were observed at temperatures below 0 °C. The optimal reaction time depends on the character of the nitrating agent, the solvent, and the reaction temperature.

As mentioned above, the nitration of NA depends substantially on the nature of the nitryl salts. Thus, the nitration of NA with NHP and NP under the conditions that are optimal for NTFB and NFS (in MeCN at 0—−40 °C), does not practically afford DNA. However, when CH_2Cl_2 is used as the solvent, the synthesis of DNA in satisfactory yields is possible (27—44 %).

Experimental

The UV spectra were recorded with a Perkin-Elmer R-12 instrument.

General procedure of nitration. NA (0.5 g) and then a stoichiometric amount of nitryl salt were added to anhydrous MeCN (10 mL) (or anhydrous CH_2Cl_2 (30 mL)) with vigorous stirring at the temperature chosen. The reaction mixture was stirred (reaction time see in Table 1), then a *ca.* 20 % solution of KOH in EtOH was added at the same temperature to make a basic medium. The mixture obtained was diluted with water and the content of the DNA anion was determined by spectral methods.

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