Soviet-era science, translated into English

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1961

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Fig. 1. IR absorption spectra of nitroform and deuteronitroform

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Abstract

Full Text

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SYNTHESIS AND SPECTRA OF DEUTERONITROFORM

(Presented by Academician A. V. Topchiev, May 5, 1961)

Trinitromethane (nitroform), being a strong acid, readily reacts with conjugated unsaturated compounds: aldehydes ([1]), ketones ([1], [2]), acids and their esters ([1]), nitriles ([1]), and vinyl ethers ([3]). In the reaction of nitroform with 2-nitroalkenes ([4]), aci-1,1,1,3-tetranitroalkanes can be isolated quantitatively.

Table 1

Compound	m.p., °C	b.p., °C/mm	n_D^{30}	d_4^{30}
$(O_2N)_3CH$	26.5 ([3])	48/15	1.4448	1.6136
$(O_2N)_3CD$	27.4–27.6	43/10	1.4430	1.6173

For a detailed study of the addition reactions of nitroform, and also for the investigation of tautomeric transformations of acinitroalkanes, it seemed of interest to us to apply the method of labeled atoms. For this purpose, deuteronitroform was synthesized by the action of dry deuterium chloride on a suspension of the potassium salt of trinitromethane in methylene chloride:

$$(O_2N)_3CK + DCl \rightarrow (O_2N)_3CD + KCl.$$

The deuteronitroform obtained consists of colorless hygroscopic crystals with m.p. 27.4–27.6°. The isotopic content of the deuterated product, determined mass-spectrographically, is 98.5%. Deuteronitroform differs little in its physical constants from ordinary nitroform. Table 1 gives comparative physical properties of deuteronitroform and nitroform obtained analogously from the potassium salt of trinitromethane and dry hydrogen chloride.

Fig. 1. IR absorption spectra of nitroform and deuteronitroform

Raman spectra (on an ISP-51 spectrograph) and IR spectra (on a UR-10 spectrometer) were recorded for deuteronitroform and ordinary nitroform. The data obtained are given in Table 2 and in Fig. 1.

As is seen from the spectra presented, both compounds have a common band at 830—833 cm^{-1}, characterizing the stretching vibrations of the C—N bond, as well as absorption bands at 1600—1608 and 1305—1310 cm^{-1}, which are attributable to respectively to the antisymmetric and symmetric stretching vibrations of the trinitromethyl group. In addition, in the spectra of deuteronitroform there is a strong band at 2266-2270 cm^{-1} of the stretching vibrations of the carbon—deuterium (C—D) bond. It should be noted that the spectral data obtained are of considerable interest for the calculation and detailed assignment of the vibrational frequencies of the trinitromethyl grouping.

Table 2

$(O_2N)_3CH$, Raman spectrum, cm^{-1}	$(O_2N)_3CH$, IR spectrum, cm^{-1}	$(O_2N)_3CD$, Raman spectrum, cm^{-1}	$(O_2N)_3CD$, IR spectrum, cm^{-1}	$(O_2N)_3CH$, Raman spectrum, cm^{-1}	$(O_2N)_3CH$, IR spectrum, cm^{-1}	$(O_2N)_3CD$, Raman spectrum, cm^{-1}	$(O_2N)_3CD$, IR spectrum, cm^{-1}
213(1)		202(1)		1305(6)	1305	1310(4 br)	1310
376(5)		374(3)		1370(4)	1370	1374(3 br)	1374
401(3 br)		391(2 br)		1408(1)		1408(0)	
415(3 br)		408(3 br)		1608(4 br)	1600	1602(2 br)	1605
570(1)	570		566	1623(4 br)		1622(2 br)	
		602(2)	605		2612	2266(1)	2270
625(2)	625		708		2670		2612
	708	750(6 br)	750	2837(1)			2670
777(2)	773		770		2902		2902
833(4)	833	833(3)	830			2972(0)	
		868(1)	865		3033		3033
		926(4)	925	3042(3)			
948(10)	944		945				
		1062(2 br)	1065				
1251(3 br)	1251						

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Experimental Part

Preparation of deuteronitroform. In a four-necked flask equipped with a sealed stirrer, a thermometer, a reflux condenser with a calcium chloride tube, and a bubbler, 47.8 g (0.5 mole) of freshly prepared dry potassium salt of trinitromethane (^{5}) was suspended in 250 ml of dry methylene chloride. Dry deuterium chloride, obtained by the method of Brown and Groot (^{6}) from 4 ml of heavy water (containing 99.97% D_2O) and 100 g of benzoyl chloride, was passed into the stirred mixture at room temperature until the yellow color disappeared. All subsequent operations, because of the hygroscopicity of deuteronitroform, were carried out in a box in an atmosphere of dry nitrogen. The reaction mixture was filtered under pressure of dry nitrogen through a glass filter into a 0.5-liter round-bottom flask, and the precipitate was washed with 50 ml of dry methylene chloride. The solvent was removed by evaporation in vacuum at 15–20 mm on a warm (30–35°) bath, and the residue was distilled from a Favorskii flask. A fraction of deuteronitroform with b.p. 43°/10 mm was collected as a colorless liquid, which solidifies to a crystalline mass upon seeding or upon freezing. Yield 30.4 g (80% of theoretical), m.p. 27.4–27.6° (from hexane with freezing), n_D^{30} 1.4430 and d_4^{30} 1.6173.

Found, %: C 8.17; 8.21; D 1.31; 1.66; N 27.83; 27.95
CN_3O_6D. Calculated, %: C 7.90; D 1.32; N 27.65

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Received
5 V 1961

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