

## A new type of the dinitrogen pentoxide–acid interaction

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DOI: 10.1016/j.mencom.2017.07.011

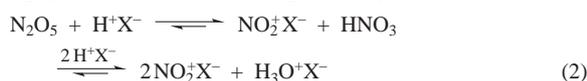
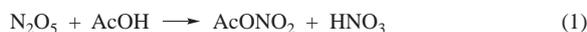
**Dinitrogen pentoxide solution in trifluoroacetic acid simultaneously has features of both known types of its interaction with acids, viz. with weak and strong acids. It partially reacts with CF<sub>3</sub>COOH to give the covalent trifluoroacetyl nitrate and nitric acid, however the major part of N<sub>2</sub>O<sub>5</sub> exists in the covalent form in solution to concurrently produce nitronium ions due to the presence of HNO<sub>3</sub>. Quantum chemical calculations confirm the equilibrium nature of CF<sub>3</sub>COOH–N<sub>2</sub>O<sub>5</sub> interaction.**



Dinitrogen pentoxide is an important reagent widely used for nitration of organic compounds<sup>1–4</sup> and for the synthesis of inorganic anhydrous nitrates<sup>5,6</sup> and nitronium salts.<sup>1,7</sup> Solid N<sub>2</sub>O<sub>5</sub> has an ionic structure [NO<sub>2</sub><sup>+</sup>][NO<sub>3</sub><sup>-</sup>],<sup>8</sup> while in the gas phase<sup>9,10</sup> and in organic solutions (Table 1) it is a covalent compound. The Raman spectra of these solutions do not exhibit an analytical line of the nitronium cation (~1400 cm<sup>-1</sup>).<sup>11</sup>

Dinitrogen pentoxide reacts with weak carboxylic acids such as AcOH to give the corresponding mixed anhydrides [equation (1)]. The reaction of HNO<sub>3</sub> with excess Ac<sub>2</sub>O also affords AcONO<sub>2</sub>, and the reaction mixture does not contain NO<sub>2</sub><sup>+</sup> cation.<sup>10–12</sup> We also did not detect NO<sub>2</sub><sup>+</sup> in the mixture resulting from N<sub>2</sub>O<sub>5</sub> dissolution in excess AcOH (see Table 1, Figure S1, Online Supplementary Materials). The Raman spectrum of the solution of equimolar amounts of molecular HNO<sub>3</sub> and AcONO<sub>2</sub> contained a single ν<sub>NO<sub>2</sub></sub><sup>s</sup> line (symmetric stretching mode of the NO<sub>2</sub> group) at 1304 cm<sup>-1</sup>.

In solutions of strong acids, N<sub>2</sub>O<sub>5</sub> showed the highest nitrating power owing to NO<sub>2</sub><sup>+</sup> ions, which were formed in these mixtures<sup>13–15</sup> [equation (2), Table 1]. This is the second type of the N<sub>2</sub>O<sub>5</sub>–acid interaction. To reach complete ionisation of N<sub>2</sub>O<sub>5</sub> to give NO<sub>2</sub><sup>+</sup> species according to equation (2), at least three equivalents of strong anhydrous acid are needed.



It was established<sup>11</sup> that in organic solutions, trifluoroacetyl nitrate (TFAN) existed in the molecular form rather than as the ionic structure [NO<sub>2</sub><sup>+</sup>][CF<sub>3</sub>COO<sup>-</sup>] (see Table 1). In the Raman spectra of TFAN solutions, the ν<sub>NO<sub>2</sub></sub><sup>s</sup> mode had a frequency of 1339–1343 cm<sup>-1</sup> and no line at 1400 cm<sup>-1</sup> for the nitronium cation was present. The <sup>14</sup>N NMR spectra of organic solutions of TFAN exhibited the nitrogen chemical shift δ<sub>N</sub> at ca. –80 ppm [for trifluoroacetic acid (TFA) solution, this chemical shift is –84 ppm]; this value was much closer to those for covalent N<sub>2</sub>O<sub>5</sub> (–62 ppm)<sup>11</sup> than to those for nitronium salts (ca. –130 ppm).<sup>16–18</sup>

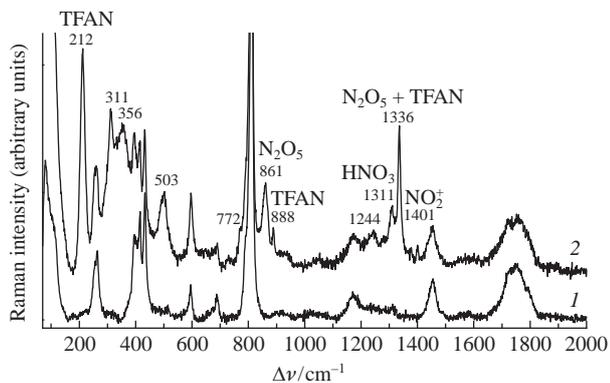
**Table 1** Raman line frequencies of the NO<sub>2</sub> group of compounds and their solutions.

Substance	Solvent or reactant (molar ratio)	The observed ν <sub>NO<sub>2</sub></sub> <sup>s</sup> values/cm <sup>-1</sup> (assignment)	Reference
HNO <sub>3</sub>	AcOH (4 : 1)	1303 (HNO <sub>3</sub> )	11
	TFA (1 : 1–4 : 1)	1306–1307 (HNO <sub>3</sub> )	11
	HNO <sub>3</sub> (neat)	1294 (vs, HNO <sub>3</sub> ), 1400 (m, NO <sub>2</sub> <sup>+</sup> )	14
	H <sub>2</sub> SO <sub>4</sub> (excess)	1400 (NO <sub>2</sub> <sup>+</sup> )	19, 20
AcONO <sub>2</sub> <sup>a</sup>	Neat	1309	11
N <sub>2</sub> O <sub>5</sub>	CHCl <sub>3</sub>	1335	9
	Solid	1397 (NO <sub>2</sub> <sup>+</sup> ), 1395 (NO <sub>2</sub> <sup>+</sup> )	8, 11
TFAN <sup>b</sup>	TFA (1 : 1–4 : 1)	1340	11
	MeNO <sub>2</sub> (2 : 1)	1343	11
N <sub>2</sub> O <sub>5</sub>	AcOH (4 : 1) <sup>c</sup>	1304 (HNO <sub>3</sub> + AcONO <sub>2</sub> )	This work
	HNO <sub>3</sub> (≥ 8 : 1)	1400 (NO <sub>2</sub> <sup>+</sup> )	15, 21
	H <sub>2</sub> SO <sub>4</sub> (9 : 1)	1401 (NO <sub>2</sub> <sup>+</sup> )	13
	H <sub>2</sub> SO <sub>4</sub> (2.3 : 1)	1315 (HNO <sub>3</sub> ), 1402 (s, NO <sub>2</sub> <sup>+</sup> )	13
	TFA (2.5 : 1) <sup>c</sup>	1311 (m, HNO <sub>3</sub> ), 1336 (s, N <sub>2</sub> O <sub>5</sub> + TFAN), 1401 (w, NO <sub>2</sub> <sup>+</sup> )	This work
	TFA (4 : 1–8 : 1) <sup>d</sup>	~1312 (m, HNO <sub>3</sub> ), ~1337 (s, N <sub>2</sub> O <sub>5</sub> + TFAN), 1403 (w, NO <sub>2</sub> <sup>+</sup> )	This work

<sup>a</sup>Prepared by dissolving N<sub>2</sub>O<sub>5</sub> in Ac<sub>2</sub>O (1 : 1, 5 °C, 24 h).<sup>5,11</sup> <sup>b</sup>Prepared from N<sub>2</sub>O<sub>5</sub> and TFAA (1 : 1.2, 5 °C, 24 h); the equimolar TFAN–TFA mixture was prepared from HNO<sub>3</sub> and TFAA (1 : 1). <sup>c</sup>In 3 h (20 °C) after dissolution (Figure 1). <sup>d</sup>In 0.5 h (0–5 °C) after dissolution.

We found that δ<sub>N</sub> –62 ppm for N<sub>2</sub>O<sub>5</sub> in TFA (2–4 mol excess) was retained only in freshly prepared solutions. In CF<sub>3</sub>COOD, this signal broadened from 25 to 40 Hz and shifted to –66 ppm within 0.5 h (5 °C) after N<sub>2</sub>O<sub>5</sub> dissolution. The observed changes pointed to occurrence of a reaction between CF<sub>3</sub>COOD and N<sub>2</sub>O<sub>5</sub>. We believe that partial formation of TFAN and NO<sub>2</sub><sup>+</sup> took place, as was confirmed by Raman spectroscopy.

In 0.5 h after N<sub>2</sub>O<sub>5</sub> dissolution in TFA (4 : 1–8 : 1), the Raman spectrum of the mixture showed lines at ~1337 (N<sub>2</sub>O<sub>5</sub> + TFAN) and ~1312 cm<sup>-1</sup> (HNO<sub>3</sub>) (see Table 1). The appearance of charac-



**Figure 1** Raman spectrum of (1) TFA and (2) the  $\text{N}_2\text{O}_5$ -TFA mixture (2.5:1), 3 h after  $\text{N}_2\text{O}_5$  dissolution.

teristic frequencies of TFAN, including the most intense line at  $\sim 213\text{ cm}^{-1}$ , confirmed the presence of TFAN<sup>11</sup> in the solution. Note that a weak  $\text{NO}_2^+$  line ( $1402 \pm 1\text{ cm}^{-1}$ ) was also observed. A similar spectral pattern was obtained in 3 h after  $\text{N}_2\text{O}_5$  dissolution in TFA (2.5:1) (Figure 1). It is noteworthy that the Raman spectrum of the  $\text{N}_2\text{O}_5$  solution in  $\text{H}_2\text{SO}_4$  with a similar concentration (2.3:1) revealed a strong  $\text{NO}_2^+$  line (see Table 1). Another distinctive feature of the spectrum of the solution in sulfuric acid was the absence of line for the molecular  $\text{N}_2\text{O}_5$  ( $\sim 1335\text{ cm}^{-1}$ ), which was detected in TFA solutions.

The differences between the Raman spectra of solutions of TFAN and  $\text{N}_2\text{O}_5$  in organic solvents made it possible to identify the individual components of the mixtures and estimate their approximate ratios. The lines at  $\sim 890$  and  $\sim 1280\text{ cm}^{-1}$  characterised the TFAN spectrum,<sup>11</sup> whereas those at  $\sim 860$  and  $\sim 1240\text{ cm}^{-1}$  belonged to molecular  $\text{N}_2\text{O}_5$ .<sup>11,14,22</sup> In the Raman spectra of TFA solutions of  $\text{N}_2\text{O}_5$ , the lines characteristic of covalent  $\text{N}_2\text{O}_5$  were much more intense than those of TFAN formed; this fact meant that the starting  $\text{N}_2\text{O}_5$  predominated in the solution. The  $\text{N}_2\text{O}_5$ :TFAN ratio did not change for several hours in all of the prepared TFA solutions of  $\text{N}_2\text{O}_5$ , thus indicating that the equilibrium had established [equation (3)]. The equilibrium nature of the reaction was ascertained by quantum chemical calculations: the Gibbs free energy for  $\text{N}_2\text{O}_5$  transformation into TFAN and  $\text{HNO}_3$  upon the reaction with TFA was found to be  $-81\text{ cal mol}^{-1}$  and the equilibrium constant was  $\sim 1.08$ .

The difference between the reaction of  $\text{N}_2\text{O}_5$  with weak organic acid that gave  $\text{AcONO}_2$  and  $\text{HNO}_3$  [equation (1)] and the reaction in question [equation (3)], where the equilibrium is shifted towards the starting  $\text{N}_2\text{O}_5$ , is worthy of note.



It is of importance that a weak characteristic  $\text{NO}_2^+$  line appeared in all Raman spectra of  $\text{N}_2\text{O}_5$  solutions in TFA (2.5:1–8:1) almost immediately after dinitrogen pentoxide dissolution. However, no nitronium cations were reliably detected after TFAN dissolution in TFA (see Table 1). There is another evidence of weak ionising ability of TFA. No  $\text{NO}_2^+$  signal in the  $^{14}\text{N}$  NMR spectra of the trifluoroacetic anhydride (TFAA)-TFAN mixture prepared by careful distillation of a TFAA- $\text{NH}_4\text{NO}_3$  mixture followed by dissolution in TFA was observed.<sup>11</sup> The spectrum contained the only TFAN signal at  $-84\text{ ppm}$ .

It is known that the  $\text{NO}_2^+$  concentration in  $\text{N}_2\text{O}_5$ - $\text{HNO}_3$  mixtures linearly depends on the portion of  $\text{HNO}_3$ ;<sup>15</sup> however, here changing the TFA: $\text{N}_2\text{O}_5$  ratio from 2.5:1 to 8:1 did not affect Raman line intensity of the nitronium cation. The line intensity ratio of covalent ( $\sim 1336\text{ cm}^{-1}$ ) and ionic ( $\sim 1402\text{ cm}^{-1}$ ) forms of  $\text{N}_2\text{O}_5$  evidences that a greater part of diluted  $\text{N}_2\text{O}_5$  in excess TFA remained unreacted and had a molecular structure. These facts also confirm a poor ionising ability of TFA as

compared to nitric and sulfuric acids (Table 1). Evidently, in TFA solutions molecular  $\text{N}_2\text{O}_5$  transforms into nitronium species basically due to nitric acid formed [equation (2),  $\text{X} = \text{NO}_3$ , see refs. 15, 22, 23].

Nitronium salts did not react with TFA<sup>24</sup> [equation (4)]. The  $^{14}\text{N}$  NMR shifts ( $-131 \pm 1\text{ ppm}$ ) of a number of nitronium salts ( $\text{NO}_2\text{ClO}_4$ ,  $\text{NO}_2\text{BF}_4$ ,  $\text{NO}_2\text{SO}_3\text{CF}_3$ , and  $\text{NO}_2\text{SO}_3\text{F}$ ) in TFA were typical of the nitronium ion and the signals of TFAN were absent.



Trifluoroacetic acid is weaker than  $\text{HNO}_3$ , therefore it is unable to generate the ionic structure  $[\text{NO}_2^+][\text{CF}_3\text{COO}^-]$  from  $\text{N}_2\text{O}_5$ , yet it is not as weak as e.g.  $\text{AcOH}$  to undergo nitration by nitronium salts [see equation (4)]. At the same time, ionisation of  $\text{N}_2\text{O}_5$  occurred due to the formation of  $\text{HNO}_3$  from the TFA- $\text{N}_2\text{O}_5$  interaction [see equations (3) and (2),  $\text{X} = \text{NO}_3$ ]. These unusual properties make TFA preferred over other solvents for successful nitration with the use of dinitrogen pentoxide and nitronium salts.

This work was supported by the Russian Foundation for Basic Research (project nos. 16-03-00713 and 16-29-01042-ofi\_m). We are grateful to Dr. M. I. Struchkova for  $^{14}\text{N}$  NMR spectra.

#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.07.011.

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Received: 3rd March 2017; Com. 17/5192