Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2004, 14(5), 197–199

Mendeleev
Communications

Catalytic vapour-phase hydrolysis and photocatalytic oxidation of dimethyl methylphosphonate on a TiO_2 surface

Dmitry A. Trubitsyn* and Alexander V. Vorontsov

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation.
Fax: +7 3832 33 1617; e-mail: tda@catalysis.nsk.su

DOI: 10.1070/MC2004v014n05ABEH001909

The products of dimethyl methylphosphonate (DMMP) hydrolysis and photocatalytic oxidation on TiO_2 were identified and quantified by a FTIR technique at different relative air humidities and concentrations of DMMP.

The development of efficient and safe methods for the decontamination of air containing chemical warfare agents is of importance.

Dimethyl methylphosphonate (DMMP) is a widely used simulant for chemical warfare agents, such as sarin and soman since the DMMP molecule contains P=O, P–O–C and P–Me moieties, which are typical of many chemical warfare agents.[1] It is believed that the absence of the P–F bond from DMMP only reduces its reactivity in comparison with that of sarin and soman since this bond undergoes fast hydrolysis.

Only few studies were devoted to the gas-phase decomposition of DMMP over polycrystalline TiO_2 at room temperature.[2–4] It is believed that the DMMP molecule is adsorbed on the TiO_2 surface *via* the interaction of the phosphoryl oxygen P=O with hydroxyl groups or titanium atoms.[3–5] At a temperature higher than 214 K, adsorbed DMMP undergoes hydrolysis with the formation of adsorbed methanol: $C_3H_9PO_3 + H_2O \rightarrow C_2H_6O_2POH + MeOH$. The photocatalytic oxidation of DMMP results in adsorbed and gaseous CO_2, CO and H_2O, as well as phosphorus-containing species, on the surface: $C_3H_9PO_3 + O_2 \rightarrow H_3PO_4 + CO_2 + CO + H_2O$.[2,4]

We studied the kinetics of DMMP hydrolysis and photocatalytic oxidation after the completion of hydrolysis on the TiO_2 surface in a batch reactor by *in situ* FTIR spectroscopy with the quantitative analysis of surface and gas-phase compounds. The influence of air relative humidity and the total quantity of DMMP present in the reactor was elucidated.

Experiments were carried out in a thermostated 300 ml reactor equipped with a 160 °C evaporator, which allowed us to evaporate injected liquid DMMP in less than 2 min. The reactor temperature was 300 K in all the experiments. TiO_2 Hombifine N was deposited on a calcium fluoride window from an aqueous suspension. All other surfaces inside the reactor were free of TiO_2. The surface density of deposited TiO_2 was 2 mg cm^{-2}, the total weight of TiO_2 was 6 mg. A DRSh-1000 mercury lamp was used for UV irradiation. The UV-light ($\lambda < 390$ nm) intensity at the photocatalyst surface was about 0.2 W cm^{-2}. The experimental setup allowed us to measure the IR spectra of species adsorbed on TiO_2 and gas-phase compounds during a single experiment by removing the TiO_2 from an IR beam without opening the reactor.

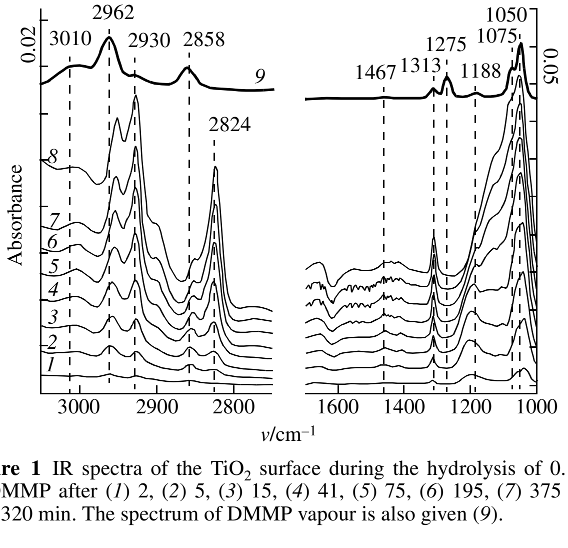

Figure 1 IR spectra of the TiO_2 surface during the hydrolysis of 0.1 µl of DMMP after (*1*) 2, (*2*) 5, (*3*) 15, (*4*) 41, (*5*) 75, (*6*) 195, (*7*) 375 and (*8*) 1320 min. The spectrum of DMMP vapour is also given (*9*).

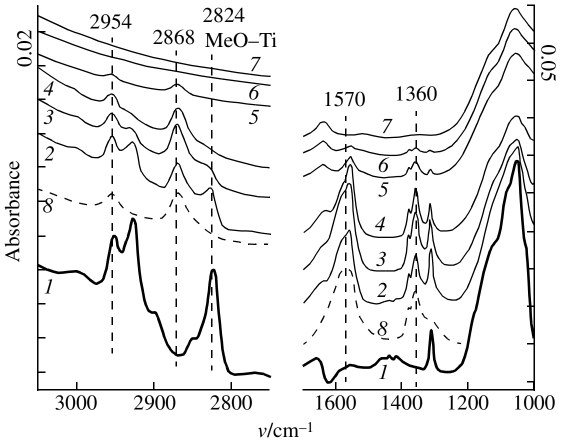

Figure 2 IR spectra of the TiO_2 surface during the photocatalytic oxidation after the completion of hydrolysis of 0.1 μl of DMMP after (*1*) 0, (*2*) 1, (*3*) 2, (*4*) 4, (*5*) 10, (*6*) 14 and (*7*) 30 min. For comparison, the spectrum of adsorbed formic acid is also given (*8*).

Before the experiments, the TiO_2 sample inside the reactor was exposed to UV light with purging air at room temperature for several hours until its FTIR spectrum became constant. The hydrolysis and photocatalytic oxidation were carried out at 1 and 50% initial relative humidities at 300 K; the DMMP quantity was 0.1 or 5 μl.

In the experiment with 1% relative humidity, after the injection of 0.1 μl (0.11 mg, 0.92 μmol) of liquid DMMP into the reactor, its full evaporation finished in about 1 min. Then, the gas-phase DMMP concentration exponentially decreased below the detection limit with the first-order reaction constant $k = 0.071$ min^{-1}. No gaseous hydrolysis products were observed; thus, all the products were adsorbed on the TiO_2 surface. The IR spectra of the TiO_2 surface are shown in Figure 1.[†,3,6,7] A band at 2824 cm^{-1} corresponds to the stretching vibrations of the MeO–Ti moiety of adsorbed methanol that is formed in DMMP hydrolysis.[3] The quantity of adsorbed methanol grows according to an exponential law with the first-order reaction rate constant $k = 4.2\times10^{-3}$ min^{-1}. It takes about 700 min for the hydrolysis to finish and by that time the adsorbed methanol quantity is equal to the initial DMMP quantity within the experimental accuracy (±10%).

To prove that the DMMP adsorption and hydrolysis take place on the TiO_2 surface only, an experiment was carried out under the above conditions without TiO_2 inside the reactor. This experiment showed that, after evaporation, the DMMP concentration in the gas phase remains constant.

To prove that hydrolysis involves mainly only one methoxy group of the DMMP molecule, hydrolysis products were washed off the TiO_2 surface with water and dimethyl sulfoxide and analysed by GC-MS. This analysis showed that, in addition to main hydrolysis products, methanol and DMMP with one methoxy group hydrolysed, trace DMMP with both methoxy groups hydrolysed occurred on the TiO_2 surface.

After the hydrolysis of 0.1 μl of DMMP was completed, the TiO_2 surface was exposed to UV radiation. The photocatalytic oxidation of adsorbed products started and the CO_2 quantity in the gas phase increased from zero to 3 μmol with the first-order reaction rate constant $k = 0.28$ min^{-1}. The final amount of CO_2 equals to the triple amount of initial DMMP within the experimental accuracy (±10%).

The TiO_2 surface spectra during the photocatalytic oxidation are shown in Figure 2. The spectrum of the TiO_2 surface exposed to UV light for 1 min can be approximated by the sum of the TiO_2 surface spectrum before photocatalytic oxidation and the spectrum of adsorbed formic acid that was exposed to UV light for 1 min. The spectrum of adsorbed formic acid was obtained in a separate experiment. A band at 1570 cm^{-1} corresponds to asymmetric COO stretching vibrations, and a band at 1360 cm^{-1} corresponds to symmetric COO stretching vibrations for bridging formate.[8] In the high-frequency region, bands at 2954 and 2868 cm^{-1} most likely correspond to O–H and C–H stretching vibrations. Thus, the photocatalytic oxidation of DMMP proceeds *via* formic acid mainly in a bridging bidentate form. Formic acid appears after 1 min oxidation and undergoes almost total oxidation into H_2O and CO_2 in 15 min. Phosphoric acid was found as the final surface product of the photocatalytic oxidation of DMMP.

In an experiment at 1% relative humidity and an excess of DMMP, after the evaporation of 5 μl (5.7 mg, 46 mmol) of liquid DMMP, vapour-phase DMMP underwent exponential decay ($k = 0.071$ min^{-1}) to the value of 12 μmol, which corresponds to the adsorption of 4.2 mg of DMMP. Gaseous methanol grew up to 1.8 μmol, which corresponds to the hydrolysis of 0.2 mg of DMMP. The total methanol quantity increased with the reaction rate constant $k = 0.0077$ min^{-1}. The maximum adsorbed methanol amount was observed at $t = 5$ min and was equal to 0.4 μmol, whereas after $t = 15$ min adsorbed methanol was not observed. Therefore, DMMP from a gas phase replaces methanol adsorbed on the TiO_2 surface; however, not all the adsorbed DMMP undergoes hydrolysis.

After the photocatalytic oxidation was started, the total DMMP quantity and methanol concentration that had formed in hydrolysis decreased, the gas phase CO_2 and CO concentration, as well as the total formic acid quantity, increased (Figure 3). DMMP displaces into the gas phase surface intermediate photocatalytic oxidation products such as formic acid and CO. Total carbon amount in the gas phase made up 25% of the total carbon amount present in the system.

To study the influence of humidity, the hydrolysis and photocatalytic oxidation of 0.1 μl of DMMP were carried out at a 50% relative humidity. After the evaporation, gaseous DMMP underwent an exponential decay ($k = 0.05$ min^{-1}) until its consumption below the detection limit. In contrast to low humidity hydrolysis, gaseous methanol was formed and its concentration exponentially increased ($k = 0.0036$ min^{-1}) until it became equal to the initial DMMP amount. A negligible amount of methanol was detected on the TiO_2 surface. Hence, water replaces methanol adsorbed on the TiO_2 surface. After UV light was turned on and photocatalytic oxidation started, the gas-phase CO_2 concentration exponentially increased ($k = 0.25$ min^{-1}). The final quantity of CO_2 was equal to the triple initial DMMP amount within the experimental accuracy. Gas-phase methanol exponentially decreased ($k = 0.33$ min^{-1}) until its total consumption.

This study demonstrated the rapid DMMP removal from a gas phase, the subsequent hydrolysis to the bonded products and total mineralization under UV radiation on the TiO_2 surface. Water was shown to displace the DMMP hydrolysis

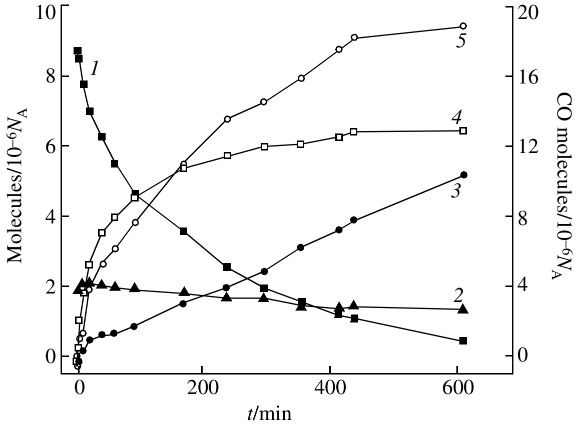

Figure 3 Changes of gas-phase compound quantities during the photocatalytic oxidation of 5 μl of previously hydrolysed DMMP: (*1*) DMMP, (*2*) methanol, (*3*) formic acid, (*4*) CO_2 and (*5*) CO.

[†] Assignment of the IR bands in the spectra of DMMP and adsorbed methanol (cm^{-1}): 3010 [ν_a(MeP)], 2962 [ν_a(MeO)], 2930 [ν_s(MeP)], 2858 [ν_s(MeO)], 2824 (MeO–Ti), 1467 [δ_s(MeO)], 1313 [δ(MeP)], 1275 [ν(P=O)], 1188 [ρ(MeP)], 1075 [ν_a(C–O)], 1050 [ν_s(C–O)].

product methanol into a gas phase. If a high concentration of DMMP is oxidised and hydrolysed, DMMP displaces hydrolysis and photocatalytic oxidation products from the surface into the gas phase. A significant excess of TiO_2 surface adsorption sites is, therefore, important for complete DMMP removal from a gas phase. Among intermediate gas-phase and surface products of the photocatalytic oxidation of DMMP, formic acid was detected and quantified for the first time.

This work was supported by the Russian Foundation for Basic Research (grant nos. NSh 1484.2003.3 and 02-03-08002), the Academy of Finland Programme 'Russia in Flux' (project no. 208134) and the Russian Science Support Foundation.

References

1 A. V. Vorontsov, L. Davydov, E. P. Reddy, C. Lion, E. N. Savinov and P. G. Smirniotis, *New J. Chem.*, 2002, **26**, 732.
2 T. N. Obee and S. Satyapal, *J. Photochem. Photobiol. A: Chem.*, 1998, **118**, 45.
3 C. N. Rusu and J. T. Yates, *J. Phys. Chem. B*, 2000, **104**, 12292.
4 C. N. Rusu and J. T. Yates, *J. Phys. Chem. B*, 2000, **104**, 12299.
5 C. S. Kim, R. J. Lad and C. P. Tripp, *Sens. Actuators B*, 2001, **76**, 442.
6 E. A. Taylor and G. L. Griffin, *J. Phys. Chem. B*, 1988, **92**, 477.
7 R. R. Shagidullin, A. V. Chernova, V. S. Vinogradova and F. S. Mukhametov, *Atlas IK-spektrov fosfororganicheskikh soedinenii* (*Atlas of IR Spectra of Organophosphorus Compounds*), Nauka, Moscow, 1984 (in Russian).
8 L.-F. Liao, W.-C. Wu, C.-Y. Chen and J.-L. Lin, *J. Phys. Chem. B*, 2001, **105**, 7678.

Received: 19th February 2004; Com. 04/2235