

## Measurement of rate constant for gas-phase reaction of DDVP with OH radical by using LP-FTIR\*

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**Abstract** Pollution caused by organic pesticides has received increasing attention. Until now, studies on organic pesticides pollution are mainly focused on soil and water. For reactions of organic pesticides in gas-phase, there are very little research results reported. Using a long path quartz reactor to simulate the atmospheric reaction of dimethyl-dichloro-vinyl-phosphate(DDVP) with OH radicals, the rate constant for the reaction at room temperature is measured at  $(3.06 \pm 0.46) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  with Fourier transform infrared spectrograph. The result indicates that DDVP degrades relatively fast in the atmosphere and is unlikely to cause persistent pollution.

**Keywords:** DDVP, OH radical, LP-FTIR, rate constant.

In order to ensure agricultural harvest, organic pesticides are highly consumed in China. In 1997, organic pesticide production in China reached 352200 tons, second to USA<sup>[1]</sup>. Organic pesticides will cause severe environmental pollution while increasing agricultural productivity. When applied to crop field, only 0.1% of pesticides is used for crop's protection<sup>[2]</sup>, the rest is maintained in environment and directly threatens human's health. In 1995, pollutants are categorized in USA according to their pollution extent. Pollution caused by hazardous pesticides ranks third, only behind ozone-layer depletion and nitrogen-phosphorus pollution from non-point sources<sup>[3]</sup>. Some organic pesticides used in past, such as hexachloro-hexane (HCH) and dichloro diphenyl trichloroethane (DDT), can exist in environment for a long time due to their chemical stability; most of these compounds are hydrophobic and liposoluble, and can be accumulated through food chain and become threats to humans<sup>[4]</sup>. Most organic pesticides applied in fields can volatilize into the atmosphere and cause regional and global environmental problems through long-range transport. Now, relative high concentration of organic pesticides in Polar Regions has been detected even though no organic pesticide was ever produced and used there<sup>[5]</sup>. This indicates that organic pesticide pollution has become a global problem, and the impacts of organic pesticides is not only determined by toxicity of organic pesticides, but also by their degradation rate. Therefore, it is very important to study

the degradation reactions of organic pesticides. However, until now, studies of organic pesticide pollution are mainly concentrated on soil and water, the kinetic data of organic pesticides reaction in gas phase is very limited.

Dichlorvos (DDVP) is a widely used pesticide in China and its output was about 26000 tons in 1990<sup>[6]</sup>. In 1996, DDVP production was still over 10000 tons in China<sup>[1]</sup>. Compared to other organic pesticides, DDVP is more easily volatilized into atmosphere. But up to now, the degradation and lifetime of DDVP in the atmosphere have not been reported. In this study, by using a quartz photo-reactor with long path Fourier transform infrared spectrograph (LP-FTIR), the photolysis and the reaction of DDVP with OH radicals were simulated. The rate constant for the gas-phase reaction of DDVP with OH radical at room temperature was also measured.

### 1 Experimental methods

#### 1.1 Instruments and reagents

A Bio-Rad FTS-65A FTIR was used to measure the concentration of DDVP and styrene; a long path quartz reactor produced by Infrared Analysis Inc. Corp. was a reaction cell with a volume of 28.5 L and contained eight 40 W black lamps with the maximal wavelength of 365 nm as light sources.

DDVP (Dikma Corp., mass fraction

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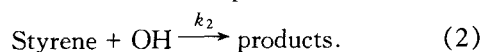
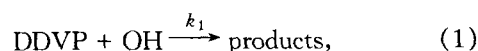
$w_1 > 99\%$ ), styrene (Beijing Fuxing Chemical Corp.,  $w_2 > 98\%$ ), high purity nitrogen and oxygen (volume fraction  $\phi > 99.99\%$ ), sodium nitrite (A. R.) and sulfuric acid (A. R.) were from Beijing Chemistry Corp.

## 1.2 Experimental theory

The rate constant for gas-phase reaction of DDVP with OH radicals was measured as described in Ref. [7]. Styrene was chosen as a reference reagent for the following reasons: (i) the rate constant of styrene reaction with OH radicals is available from literature; (ii) styrene has very strong infrared absorption at  $909\text{ cm}^{-1}$ ; (iii) photolysis and reaction of styrene with DDVP cannot be observed under the black lamps at room temperature.

Relative rate technique is a method to measure rate constants by monitoring the disappearance of two compounds in the chemical reaction system containing OH radicals. One compound is the reference (e. g. styrene), whose rate constant with OH radicals is known, and the other is the compound whose rate constant needs to be measured (e. g. DDVP).

The reactions occurring in the reactor can be expressed as



$k_1$ ,  $k_2$  are the rate constants of Eqs. (1) and (2), respectively. Then,

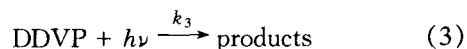
$$-\text{dln}C_1/\text{d}t = k_1 C_{\text{OH}},$$

$$-\text{dln}C_2/\text{d}t = k_2 C_{\text{OH}},$$

where  $C_{\text{OH}}$ ,  $C_1$ ,  $C_2$  are the concentrations of OH radicals, DDVP and styrene, respectively,  $t$  is the reaction time. Then

$$\ln(C_1^0/C_1^t) = k_1/k_2 \ln(C_2^0/C_2^t),$$

where  $C_1^0$  and  $C_1^t$  are the concentrations of DDVP at time 0 and  $t$ ; and  $C_2^0$  and  $C_2^t$  are the concentrations of styrene at time 0 and  $t$ . If the photolysis of DDVP is not negligible, then



where  $k_3$  is rate constant for reaction (3), then

$$\ln(C_1^0/C_1^t)/t = k_1/k_2 \{ \ln(C_2^0/C_2^t)/t \} + k_3.$$

The plot of  $\ln(C_1^0/C_1^t)/t$  against  $\ln(C_2^0/C_2^t)/t$  should yield a straight line with a slope  $k_1/k_2$  and an intercept  $k_3$ . Because  $k_2$  is known,  $k_1$  can be obtained.

## 1.3 Generation of OH radicals

The pressure in quartz chamber was reduced to lower than 133 Pa with a vacuum pump. Nitrous acid (HONO) was produced by reaction of 2 mL sodium nitrite solution ( $\text{NaNO}_2$ , 1 mol/L) with 2 mL 50%  $\text{H}_2\text{SO}_4$  in an ice-water bath, and then it was introduced into the reactor by pressure difference between the reactor and reaction flask. Afterwards, 1  $\mu\text{L}$  styrene and 1  $\mu\text{L}$  DDVP were injected into the inlet, where the temperature was increased to 70  $^\circ\text{C}$  and maintained for 15 min to volatilize styrene and DDVP. High pure oxygen and nitrogen (with a ratio of 4 : 1 in volume) were flushed into the reactor through the inlet until the pressure increased to  $1.01 \times 10^5$  Pa. When the black lamps were turned on, OH radicals were produced from the photolysis of HONO, then reacted with styrene and DDVP.

## 2 Results and discussion

### 2.1 The photolysis of DDVP

The change of DDVP concentration was observed by LP-FTIR when the black lamps were switched on. Table 1 lists the change of DDVP concentration with time at room temperature ( $23 \pm 2$ )  $^\circ\text{C}$ .

Table 1. Photolysis of DDVP with black lamps

	Time(min)								
	0	3.5	6	9	12	15	18	21	24
$C_1^t/C_1^0$	1	0.987	0.956	0.953	0.943	0.920	0.909	0.898	0.872

A plot of  $\ln(C_1^0/C_1^t)$  against time is drawn in Fig. 1.

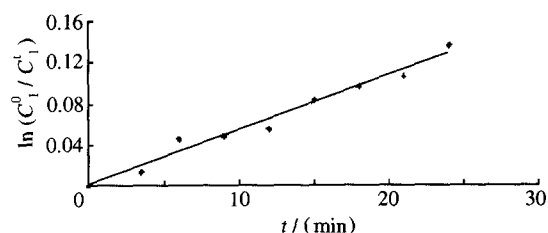


Fig. 1. The photolysis of DDVP under black lamps.

The line in Fig. 1 can be described by the equation of  $\ln(C_1^0/C_1^t) = (0.0054 \pm 0.0003) t$ , which means that under the experimental conditions the rate constant of DDVP photolysis is  $0.0054\text{ min}^{-1}$ . About 12% of DDVP was photolyzed after 20 min. So photolysis of DDVP was not negligible in the experiment that measures the rate constant for the reaction of

DDVP with OH.

## 2.2 Determination of the rate constant of DDVP reacted with OH radicals

The changes of DDVP and styrene concentrations were observed by LP-FTIR, and the results are listed in Table 2.

Table 2. Reaction of styrene and DDVP with OH radical

	Reaction time (min)								
	0	2.4	4.4	6.4	8.4	10.4	12.9	15.4	17.9
$C_2^t/C_2^0$	1	0.905	0.751	0.662	0.574	0.478	0.377	0.302	0.224
$C_1^t/C_1^0$	1	0.936	0.839	0.75	0.680	0.598	0.540	0.487	0.407

From the data of Table 2,  $\ln(C_1^0/C_1^t)/t$  vs.  $\ln(C_2^0/C_2^t)/t$  is plotted in Fig. 2.

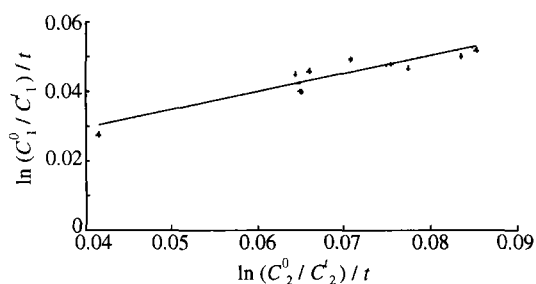


Fig. 2. DDVP and styrene reaction with OH at  $(23 \pm 2)^\circ\text{C}$ .

The line in Fig. 2 can be expressed by a linear equation  $\ln(C_1^0/C_1^t)/t = (0.54 \pm 0.07) \ln(C_2^0/C_2^t)/t + (0.007 \pm 0.005)$ , where the slope ( $k_1/k_2$ ) is 0.54 and intercept is  $0.007 \text{ min}^{-1}$ . The rate constant for gas-phase reaction of styrene with OH radical at room temperature is  $5.86 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ <sup>[8]</sup>, the rate constant for gas-phase reaction of DDVP is calculated to be  $3.16 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

This measurement was repeated three times. The results are  $2.52 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ,  $2.91 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and  $3.63 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , respectively. So the average rate constant of DDVP reaction with OH radical is  $(3.06 \pm 0.46) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at room temperature ( $23 \pm 2^\circ\text{C}$ ). Assuming the average concentration of OH radicals in the atmosphere is  $7 \times 10^5 \text{ cm}^{-3}$ <sup>[9]</sup>, the lifetime of DDVP in atmosphere is estimated to be about  $1/(3.06 \times 10^{-11} \times 7 \times 10^5) = 13 \text{ h}$ , which indicates that DDVP is unlikely to cause persistent pollution.

## 3 Conclusions

From our experimental results, some conclusions can be made here.

(i) The photolysis and reaction with OH radicals contribute greatly to the removal of DDVP in atmosphere. From our knowledge, the rate constant of DDVP that reacted with OH radicals is  $3.06 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at room temperature which is two orders of magnitude faster than the reported rate constant of hexachlorocyclohexane (HCH) that reacted with OH radicals ( $1.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ )<sup>[10]</sup>.

(ii) The lifetime of DDVP in atmosphere is estimated at about 13 hours, which is absolutely shorter than the lifetime of HCH (120 days as reported by Brubaker et al.<sup>[10]</sup>). Therefore DDVP should not cause persistent pollution as HCH does.

(iii) The rate constants for gas-phase reaction in the atmosphere provide direct evidence for organic pesticides pollution. They are very important parameters in global pollution models for organic pesticides.

In summary, the kinetics and mechanism of atmospheric degradation of organic pesticides need further investigation. It is the low vapor pressure of the most organic pesticides that makes simulation experiments difficult. The development and application of highly sensitive detectors is a key factor to this research field.

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