

**Table I : Réactions OH + dimethyl carbonate (1) and OH + diethyl carbonate (2) : summary of experimental conditions and measured  $k_1$  and  $k_2$ .**

T (K)	[dimethyl carbonate] ( $10^{14}$ ) <sup>a</sup>	$10^{13} \times (k_1 \pm 2\sigma)$ <sup>b</sup>	[diethyl carbonate] ( $10^{14}$ ) <sup>a</sup>	$10^{12} \times (k_2 \pm 2\sigma)$ <sup>b</sup>
263	2.45 - 26.87	$3.62 \pm 0.16$	-	-
273	2.61 - 26.82	$3.55 \pm 0.21$	$0.55 - 5.80$	$3.06 \pm 0.13$
283	2.52 - 27.16	$3.39 \pm 0.18$	-	-
298	2.12 - 24.35	$3.60 \pm 0.17$	$0.47 - 4.67$	$2.57 \pm 0.13$
298	2.39 - 23.14	$3.54 \pm 0.22$	$1.50 - 6.93$	$2.16 \pm 0.15$
298	2.45 - 26.04	$3.46 \pm 0.18$ <sup>c</sup>	$1.20 - 13.26$	$2.21 \pm 0.29$ <sup>d</sup>
298	4.77 - 49.54	$3.34 \pm 0.14$ <sup>e</sup>	-	-
323	2.47 - 24.14	$3.59 \pm 0.18$	-	-
333	-	-	$1.51 - 6.33$	$2.04 \pm 0.08$
348	1.77 - 20.52	$3.99 \pm 0.18$	-	-
368	-	-	$1.49 - 5.65$	$1.92 \pm 0.10$
372	1.69 - 19.00	$4.59 \pm 0.11$	-	-
372	3.22 - 35.13	$4.28 \pm 0.12$ <sup>d</sup>	-	-

<sup>a</sup> Units of molecule cm<sup>-3</sup>. <sup>b</sup> Units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>c</sup> Variation of the photolysis laser fluence (decrease by a factor of 3). <sup>d</sup> Variation of flow velocity (decrease by a factor of 3).

<sup>e</sup> Experiments carried out at 300 Torr.

**Table II : Comparison of OH reaction rate coefficients with previous Work.**

Molecule	T (K)	<sup>a, b</sup> k, 10 <sup>-12</sup>	<sup>a, b</sup> A, 10 <sup>-12</sup>	<sup>a, c</sup> E/R, K	T range, K	<sup>d</sup> technique	reference
<b>CH<sub>3</sub>OC(O)OCH<sub>3</sub></b>	298	0.315 ± 0.007	0.59 ± 0.20	(179 ± 105)	252 - 370	FP-RF	<b>Bilde <i>et al.</i> (1997)</b>
	298	0.349 ± 0.039	0.83 ± 0.27	(247 ± 98)	263 - 372	PLP-LIF	This work
<b>C<sub>2</sub>H<sub>5</sub>OC(O)OC<sub>2</sub>H<sub>5</sub></b>	298	2.31 ± 0.29	0.46 ± 0.15	- (503 ± 203)	273 - 368	PLP-LIF	This work

<sup>a</sup> Errors are those given by the authors.

<sup>b</sup> Units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

<sup>c</sup> For our data, the uncertainties for A and E/R are given by  $\Delta A = 2A \sigma_{\ln A}$  and  $\Delta E/R = 2 \sigma_{E/R}$  for the Arrhenius forms.

<sup>d</sup> Key : FP-RF, Flash Photolysis – Resonance Fluorescence. LP-LIF, Laser Photolysis-Laser Induced Fluorescence.

**Table III : Binary diffusion coefficient in gas phase at 1 atm and 298 K.**

Molecules	$D_{X-H_2O}$ (cm <sup>2</sup> . s <sup>-1</sup> )	$D_{X-He}$ (cm <sup>2</sup> . s <sup>-1</sup> )
$CH_3OC(O)OCH_3$	0.1243	0.3368
$C_2H_5OC(O)OC_2H_5$	0.1014	0.2710

**Table IV : Uptake coefficients, Henry's law constants and mass accommodation coefficients of dimethyl carbonate : Summary of Experimental Conditions.**

T (K)	$10^2 \times \gamma$ ( $2\sigma + 10\%$ )	H (M/atm) ( $2\sigma$ )	$10^2 \times \alpha$ ( $2\sigma + 10\%$ )
265.2	$0.92 \pm 0.11$	$106.7 \pm 14.6$	- <sup>2</sup>
267.6	$1.40 \pm 0.18$	$81.3 \pm 22.8$	- <sup>2</sup>
268.3 <sup>1</sup>	$0.92 \pm 0.12$	$63.3 \pm 11.4$	- <sup>2</sup>
268.8	$0.90 \pm 0.05$	$39.6 \pm 0.6$	- <sup>2</sup>
270.0	$1.38 \pm 0.23$	$22.2 \pm 12.9$	- <sup>2</sup>
270.5	$1.26 \pm 0.11$	$61.1 \pm 13.8$	$11 \pm 2$
270.6 <sup>1</sup>	$0.65 \pm 0.17$	$28.71 \pm 14$	- <sup>2</sup>
270.9	$0.07 \pm 0.005$	$20.3 \pm 15.8$	- <sup>2</sup>
273.0	$1.10 \pm 0.19$	$23.2 \pm 10.2$	$9 \pm 2$
273.2 <sup>1</sup>	$1.4 \pm 0.16$	$10.26 \pm 4.5$	- <sup>2</sup>
273.7	$1.50 \pm 0.24$	$45.1 \pm 18.5$	- <sup>2</sup>
274.2	$1.06 \pm 0.35$	$42.6 \pm 10.9$	$11 \pm 2$
274.5	$1.24 \pm 0.37$	$41.4 \pm 12.4$	- <sup>2</sup>
275.5 <sup>1</sup>	$0.50 \pm 0.19$	$26.3 \pm 8.4$	- <sup>2</sup>
276.2	$0.81 \pm 0.08$	- <sup>2</sup>	$1.2 \pm 0.9$
276.5	$1.12 \pm 0.09$	$22.8 \pm 16.7$	- <sup>2</sup>
277.2	$1.17 \pm 0.12$	$20.3 \pm 6.7$	- <sup>2</sup>
278.2	$0.86 \pm 0.04$	$50.2 \pm 14.5$	$3.3 \pm 0.3$
278.6 <sup>1</sup>	$0.73 \pm 0.11$	- <sup>2</sup>	- <sup>2</sup>
279.2	$0.66 \pm 0.16$	$20.6 \pm 4.3$	- <sup>2</sup>

<sup>1</sup> Experiments carried out using 0.1 M NaOH solution.

<sup>2</sup> The values cannot be extracted.

**Table V : Uptake coefficients, Henry's law constants and mass accommodation coefficients of diethyl carbonate : Summary of Experimental Conditions.**

T (K)	$10^2 \times \gamma$ ( $2\sigma + 10\%$ )	H (M/atm) ( $2\sigma$ )	$10^2 \times \alpha$ ( $2\sigma + 10\%$ )
270.3	$1.30 \pm 0.22$	$97.8 \pm 14.6$	$9.4 \pm 3.0$
270.6 <sup>1</sup>	$0.11 \pm 0.02$	$99.9 \pm 14.9$	- <sup>2</sup>
271.0	$2.36 \pm 0.17$	$56.1 \pm 8.2$	$14.2 \pm 2.7$
272.3	$2.03 \pm 0.34$	$83.0 \pm 13.5$	- <sup>2</sup>
273.3 <sup>1</sup>	$0.25 \pm 0.05$	$48.8 \pm 12.8$	- <sup>2</sup>
273.6	$0.95 \pm 0.29$	$68.9 \pm 26.8$	$1.8 \pm 0.5$
273.8	$0.92 \pm 0.04$	$14.7 \pm 5.6$	- <sup>2</sup>
275.5	$0.89 \pm 0.12$	$59.0 \pm 14.7$	$6.1 \pm 2.7$
275.5 <sup>1</sup>	$0.14 \pm 0.04$	$36.5 \pm 12.5$	- <sup>2</sup>
277.5	$1.6 \pm 0.26$	$38.7 \pm 8.5$	- <sup>2</sup>
278.8 <sup>1</sup>	$0.09 \pm 0.02$	$50.23 \pm 14.8$	$1.4 \pm 0.6$
278.9	$1.20 \pm 0.24$	$30.6 \pm 12.8$	- <sup>2</sup>

<sup>1</sup> Experiments carried out using 0.1 M NaOH solution.

<sup>2</sup> The values cannot be extracted.

**Table VI : Entropy and Enthalpy Values for dimethyl and diethyl carbonate.**

Compound	$\Delta S_{\text{obs}}$ (cal mol <sup>-1</sup> K <sup>-1</sup> ) <sup>1</sup>	$\Delta H_{\text{obs}}$ (kcal mol <sup>-1</sup> ) <sup>1</sup>
Dimethyl carbonate	-99 ± 35	- 26 ± 9
Diethyl carbonate	- 137 ± 38	- 36 ± 11

<sup>1</sup> The errors correspond to  $1\sigma$ .