

## IR LASER DRIVEN DECOMPOSITION OF OXALYL CHLORIDE IN PRESENCE OR RADICAL SCAVENGERS: EVIDENCE FOR MOLECULAR MECHANISM

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CO<sub>2</sub> laser-induced and SF<sub>6</sub> (0.4–0.5 kPa) sensitized decomposition of oxalyl chloride (4 kPa) in the presence of radical scavengers (2.6–8.7 kPa) as hydrogen, propene and nitric oxide obeys first-order kinetics and is supportive of the view that oxalyl chloride thermally decomposes by concerted molecular mechanism.

The thermal decomposition of oxalyl chloride yielding carbonyl chloride and carbon monoxide is, based on the kinetic results, viewed<sup>1</sup> as a nearly completely homogeneous chain reaction incorporating transient occurrence of Cl atoms and <sup>•</sup>COCl radicals. The species were, however, not detected<sup>2</sup> by matrix IR spectroscopy of decomposition products which doubts the radical mechanism proposed.

Herein we report SF<sub>6</sub>-sensitized CO<sub>2</sub>-laser-induced decomposition and conventional thermolysis of oxalyl chloride in the presence of radical scavengers as nitric oxide, propene and hydrogen with the aim to elucidate both the mechanism and the role of surface reactions. The laser-inducement of a gas reaction obviates heterogeneous reaction pathways on reactor wall<sup>3</sup> and may lead to a tremendous impact upon reaction mechanism as was already proved<sup>4,5</sup>. Of the radical scavengers, hydrogen and propene react<sup>6,7</sup> with radicals *via* abstraction of their hydrogen atom, while nitric oxide is very effective in catalyzing the recombination of chlorine atoms<sup>8</sup>.

### EXPERIMENTAL

CO<sub>2</sub> laser-induced, SF<sub>6</sub>-sensitized decomposition was performed in a cylindrical stainless steel optical cell (1.4 cm long, i.d. 3.5 cm) with NaCl windows and a needle valve. A cw CO<sub>2</sub> laser operated at the P (34) line of the 00<sup>0</sup>1→10<sup>0</sup> transition with 4 W power (beam focussed with Ge lens of f. 1.25 cm into the middle of the cell) was used for the irradiation of gaseous mixtures of SF<sub>6</sub> and (COCl)<sub>2</sub> with or without the scavenger (NO, C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub>). The analysis of the concentration of the reactant (COCl)<sub>2</sub> and the product COCl<sub>2</sub> by a Perkin-Elmer Model 621 infrared spectrometer at measured intervals of the decomposition was based on the knowledge of the absorptivity of (COCl)<sub>2</sub> at 778 cm<sup>-1</sup> (ν<sub>10</sub>) and COCl<sub>2</sub> at 850 cm<sup>-1</sup> (ν<sub>4</sub>) and was performed as described<sup>5</sup>. Gas handling was carried out on a standard vacuum line.

The reaction vessel for conventional pyrolysis was a glass cylinder packed with ceramic rings and was electrically heated to 300°C.

Oxalyl chloride, propene (both Fluka A.G., Buchs), sulfur hexafluoride (Montedison Milano, I.E.C. Standard), and hydrogen (Technoplyn, Prague) were commercial products. Nitric oxide was prepared and purified according to the procedure<sup>9</sup>.

## RESULTS AND DISCUSSION

Both the conventional (see also<sup>1</sup>) and SF<sub>6</sub>-sensitized CO<sub>2</sub> laser-induced decomposition of oxalyl chloride (4 kPa) proceed according to Eq. (1)

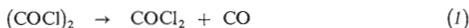


TABLE I

SF<sub>6</sub>-sensitized, CO<sub>2</sub> laser-induced decomposition of oxalyl chloride

Gas, kPa	SF <sub>6</sub> , kPa	(COCl) <sub>2</sub> , kPa	10 · k <sub>1</sub> <sup>a</sup> , s <sup>-1</sup>	COCl <sub>2</sub>
				(COCl) <sub>2</sub> decomposed
—	0.5	3.6	7.5	0.96
NO 2.5	0.5	4.1	5.0	0.98
C <sub>3</sub> H <sub>6</sub> 3.3	0.4	3.7	5.0	1.0
H <sub>2</sub> 3.3	0.4	3.6	2.0	0.97

<sup>a</sup> First-order rate constant relates to the irradiation conditions given in Experimental; <sup>b</sup> at 100% conversion.

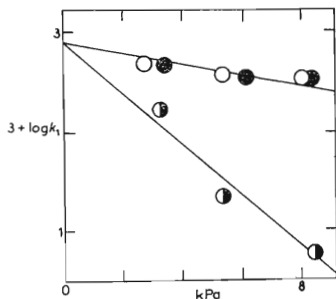


FIG. 1

The effect of added gases (kPa, NO ○, propene ●, H<sub>2</sub> ◐) upon the first-order rate constant of the SF<sub>6</sub> (0.5 kPa)-sensitized, CO<sub>2</sub> laser-induced decomposition of oxalyl chloride (4–4.1 kPa). First-order rate constant relates to the irradiation conditions given in Experimental

and are first-order reactions with the  $(\text{COCl})_2$  decomposed:  $\text{COCl}_2$  ratio equaling to unity. This ratio holds for the entire course of both conventional and laser-induced decompositions and is also unaltered (Table I) upon addition of hydrogen, propene, or nitric oxide that are efficient scavengers of  $\cdot\text{Cl}$  and  $\cdot\text{COCl}$  species, which thus disproves the radical nature of the decompositions. Apparently, the reaction exclusively takes place in the gas phase and is of a molecular mechanism. Earlier calculated<sup>1</sup> Arrhenius parameter  $\log A (\text{s}^{-1}) = 12.56$  for conventional thermal decomposition appears now to suit rather well unimolecular complex fission reaction<sup>10</sup> involving simultaneous breaking and/or making of two or more bonds.

As far as the laser-induced reaction is concerned, its rate decreases with increasing amounts of nitric oxide, hydrogen, or propene added to the  $\text{SF}_6-(\text{COCl})_2$  mixture. Representative runs are given in Table I and Fig. 1. The greatest ability to diminish the reaction rate is shown by hydrogen, perhaps due to its highest thermal conductivity. The simple kinetic equation valid for the laser process is obviously consistent with rapid relaxation time of  $\text{SF}_6$ , and the consequent rapid mixing due to convection of the gas in the cell that insure<sup>3</sup> a considerable level of chemical homogeneity.

Our data, strongly supportive of molecular mechanism for thermal decomposition of oxalyl chloride, seem to sound rather astounding in conjugation with reactions of oxalyl chloride occurring in the absence of sources of radicals or promoters of ionic reaction. The chloroformylation of certain unsaturated hydrocarbons<sup>11</sup> and heterocycles<sup>12</sup> occurring by a polar type reaction hence implies that an interaction of  $(\text{COCl})_2$  with these compounds prefers intermolecular bond reorganization over concerted  $(\text{COCl})_2$  molecular decomposition.

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