
LASER INDUCED GAS PHASE REACTION BETWEEN CHROMYL CHLORIDE AND SOME POLYHALOGENOETHENES

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Gas phase reaction between chromyl chloride and some polyhalogenoethenes induced with the radiation of continuous-wave CO₂ laser yields carbonyl halides and compounds arising from oxygen donation to alkene and 1,2-rearrangement of halogen.

Chromyl chloride is a powerful oxidizing reagent^{1,2} of organic substances and its reactions with alkenes intensively studied³⁻⁶ in the liquid phase mostly lead to multitude of products as epoxides, chlorohydrines, vicinal dichlorides and carbonyl compounds. The preference for the last compounds can be achieved by conducting the reaction at low temperatures⁷, or via reductive hydrolysis of the CrO₂Cl₂-olefin adduct⁸. These liquid-phase reactions were assumed to progress via an CrO₂Cl₂ olefin intermediate in which the 1,2-alkyl or hydrogen migration takes place to the carbon more capable of supporting a positive charge⁹. Different mechanism was forwarded on the basis of *ab initio* theoretical methods and it consists of primary interaction with olefine of only one chromyl chloride oxygen and the intermediate stabilizing interaction by the second (spectator) oxo group¹⁰.

Apart from the oxidizing ability, also the interaction of chromyl chloride with infrared laser radiation, namely infrared multiphoton production of electronically excited molecules has also been studied¹¹⁻¹⁵. There are, however, no reports on chemical reactions between this versatile oxidizing reagent and organic substances which are induced by laser radiation.

In this note we wish to report that chromyl chloride irradiated with a continuous-wave CO₂ laser beam does easily react with polyhalogenated ethenes in the gas-phase, which is, with regard to the known lack of the chromyl chloride reactivity to these olefins in the liquid phase, rather surprising.

RESULTS

Our preliminary results were achieved with a simple arrangement at pressures of chromyl chloride and olefin being 0.5–1.5 and 0.5–5 kPa, respectively. The reaction

was studied in a glass tube reactor equipped with two NaCl windows, a stopcock and a side-arm separated from the tube by PTFE joint. The mixtures of chromyl chloride and olefin were prepared by a standard vacuum-line technique. Chromyl chloride was introduced into the reactor first, it was frozen in the side-arm which was subsequently closed and thereafter olefin was admitted to fill the reactor volume. The mixture of both substances formed upon the opening of the PTFE joint was irradiated by the cw CO₂ laser tuned to the *R*(24) line of the 10.6 μm band with constant output ranging from 5 to 10 W, and with the beam focused (Ge lens, focal length 10 cm) into the center of the reactor. The *R*(24) line is absorbed in the ν_1 (symmetric Cr—O stretching) vibration of CrO₂Cl₂ at 995 cm⁻¹ (ref.¹⁶). In fact, the absorption induced by a 5-W, ~1 cm-diameter laser beam in 2.7 kPa of CrO₂Cl₂ ranges for the *R*(24)–*R*(34) lines between 0.016 and 0.018 cm⁻¹ kPa⁻¹, which shows that it is essentially independent of laser frequency within the range studied. The change in the composition of parent mixture after irradiation at measured intervals was monitored by scanning the i.r. spectra at 500–4 000 cm⁻¹ and the depletion of olefin as well as the increase in the concentration of new compounds were followed by means of characteristic absorption bands and known absorption coefficients¹⁷ of these compounds.

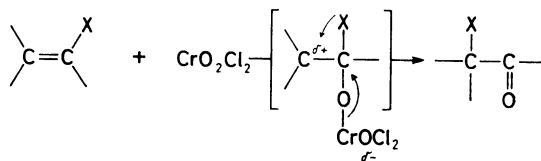
Laser induced reaction between chromyl chloride and trichloroethene yields trichloroacetaldehyde and carbonyl chloride. The reaction is favored with higher concentrations of chromyl chloride, but it yields more carbonyl chloride and less aldehyde (Table I). Typical reaction progress is given in Fig. 1. It is plausible to assume that carbonyl chloride is the product of trichloroacetaldehyde oxidation, since reaction between chromyl chloride and trichloroacetaldehyde was independently verified. By 6 minutes long irradiation (5 W laser output) of CrO₂Cl₂ (2.4 kPa)–Cl₃C.CHO (1.6 kPa) mixture the aldehyde decreased to 0.8 kPa and 0.7 kPa of carbonyl chloride was formed.

Laser induced reaction (5 W laser output) between chromyl chloride and tetrafluoroethene (both 1.1 kPa) yields trifluoroacetyl fluoride 0.35 kPa and carbonyl fluoride (0.5 kPa) when the mixture is irradiated for 20 minutes.

Similar course is also observed with laser induced chromyl chloride oxidation of 1,1- and 1,2-dichlorodifluoroethenes which yield halides COX₂ (X = Cl, F) and carbonyl compounds whose structure was tentatively assigned to CF₂Cl.CCl(O) and CFCl₂.CF(O).

These data show that gas-phase reaction between chromyl chloride and olefins with electronegative substituents can be conveniently induced by laser radiation absorbed in chromyl chloride, despite that no reaction between both species takes place in the liquid phase.

The occurrence of Cl₃C.CHO, CF₃.C(O)F and of perhaps CF₂Cl.C(O)Cl and CFCl₂.C(O)F products can be only explained by a 1,2-rearrangement of halogen as described in Scheme 1.



SCHEME 1

The results contribute to remaining effort to moderate reactivity of the strong CrO_2Cl_2 oxidant (see e.g. refs^{7,8,18}) and also show that laser absorption in CrO_2Cl_2

TABLE I
Laser induced reaction between CrO_2Cl_2 and trichloroethene^a

CHCl ₂ : CHCl kPa	CrO ₂ Cl ₂ kPa	Irradn. time min	Gaseous product, kPa	
			Cl ₃ C.CHO	COCl ₂
4.8	0.5	30	0.11	0.01
4.0	1.0	30	0.29	0.08
3.2	1.3	10	0.70	0.27

^a Laser output 10 W.

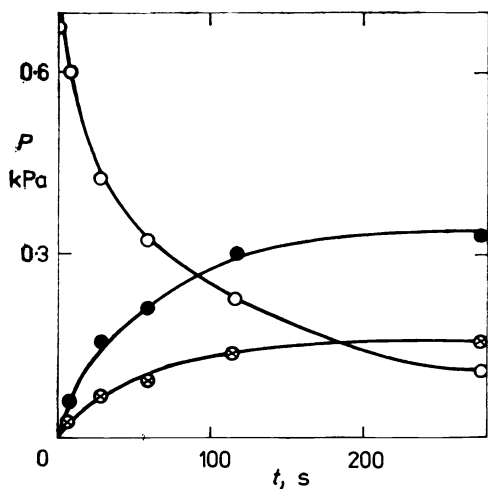


FIG. 1
Progress of laser induced (10 W) reaction between CrO_2Cl_2 (2.7 kPa) and $\text{ClHC} : \text{CCl}_2$ (0.7 kPa). The compounds designated are CrO_2Cl_2 (○), $\text{Cl}_3\text{C.CHO}$ (●), and COCl_2 (⊗)

can induce reaction that has not been until now observed to occur under other conditions. More work is in progress.

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