

Letter to the Editor

Comments on "The chlorine atom sensitized oxidation of HCCl_3 , HCF_2Cl and HCF_3 "

In the first page of his paper [1] Sanhueza states that the only work on the oxidation mechanism of hydrogen-containing halomethanes is that of Sanhueza and Heicklen [2] and that there are no data reported on the oxidation mechanisms of HCCl_3 , HCF_3 and HCF_2Cl . He has overlooked that the kinetics of the Cl atom sensitized oxidation of HCCl_3 and of HCFCl_2 were extensively studied by Schumacher and coworkers many years before [3, 4].

Schumacher and Wolff [3] investigated the oxidation of HCCl_3 between 55 and 75 °C irradiated by light of wavelength 4358 Å. In their experiments they followed the complete course of the reaction, measuring the rates throughout. The HCCl_3 pressures were varied between 3 and 160 Torr, the O_2 pressures between 3 and 450 Torr, the Cl_2 pressures between 30 and 160 Torr and the total pressures between 150 and 700 Torr; I_0 was varied by a factor of 3.

The reproducibility of the results was excellent and it was shown that the reaction was a homogeneous chain reaction producing COCl_2 and HCl as the only products. It was found that, if oxygen was present above a certain pressure limit of the order of 1 Torr, the reaction products and the total pressure had no influence on the course of the reaction. However, the quantum efficiency increased steadily with an increase of the HCCl_3 pressure. The reaction had a small positive temperature coefficient of 1.23 ± 0.05 . The experimentally determined rate equation represented all results in a quantitative way.

According to Sanhueza (page 326) the quantum yield of the COCl_2 formation increases with the HCCl_3 pressure, approaching an upper limiting value of 200, and decreases either with an increase of the light intensity or an increase of the total pressure. However, it is not clear on which experimental data these conclusions are based.

There are very few numerical values given, which are summarized in Table 2, p. 327. In all, eight experiments are presented, all performed at the same temperature of 30 ± 2 °C, and all referring to the initial rate of the reaction. This means that there are only eight "points". In each experiment several parameters were changed.

If we look at the first two experiments we find for the ratios of the different parameters the following values. For the HCCl_3 pressures $1.60/2.60 = 0.61$; for the absorbed light $0.44/0.19 = 2.3$ and for the total pressure (in experiment 1 30 Torr N_2 were present) $39.6/10.36 = 3.8$. According to

Sanhueza the quantum yield Φ of experiment 1 should be much lower than Φ of experiment 2, because in experiment 1 he had a much lower HCCl_3 pressure and much higher values for the absorbed light and the total pressure. However, we observe the reverse: $\Phi_1 = 115$ and $\Phi_2 = 105$ molecule photon⁻¹. If we compare experiments 2 and 3, we see that there is only a small difference in both CHCl_3 pressures (2.60 and 2.90 Torr), whereas the absorbed light is higher in experiment 3 by a factor of $91/19 = 4.8$ and the total pressure by a factor of 1.7. Referring to the statements of Sanhueza, Φ of experiment 3 should consequently be much lower than Φ of experiment 2. The corresponding values are, however, 110 and 105, respectively.

If we move from experiment 3 to experiment 4 we see no difference in the values for the absorbed light, a small increase of the HCCl_3 pressure from 2.90 to 3.94 Torr and a very strong increase in total pressure, from 17 to 90 Torr. Nevertheless the Φ values for both experiments are the same.

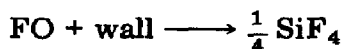
However, if we now look at experiment 5, where there is in comparison with experiment 4 only a slight increase of the HCCl_3 pressure (from 3.94 to 5.18 Torr), a strong increase of the quantum yield is observed. Φ jumps suddenly to a value of 215, and this value remains unchanged in experiments 6, 7 and 8, no matter how strongly the other parameters that might have some influence on the reaction are varied.

Therefore, from the values presented in Table 2, it must be concluded that at HCCl_3 pressures between 1.60 and 3.94 Torr independently of the values of the total pressure, O_2 and I_{abs} , a quantum yield Φ of 107 ± 7 molecule photon⁻¹ is obtained, whereas at HCCl_3 pressures above 5.18 Torr, independently of the values of the other parameters, the quantum yield Φ has a constant value of 200 ± 14 molecule photon⁻¹. Obviously this does not make sense.

On page 328 the author states that "it is well known that COF_2 decomposes heterogeneously with glass". However, considering the very high value for the C—F bond it seems to us to be highly improbable that COF_2 will react with SiO_2 . As a matter of fact, we never observed such a reaction in quartz cells, if the surface was clean enough and all traces of water had been eliminated [5].

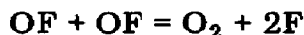
On page 333 he predicts that HCCl_2F must be oxidized in a long chain reaction having CFCIO as the exclusive oxidation product. The kinetics of this reaction were studied by Schumacher many years ago [4]. This reaction is similar to the one investigated before. However, the rate equation is somewhat different.

Finally, on page 334, in one of the proposed mechanisms the following reaction is mentioned:



with the comment that "little is known about the reactions of FO...". To this it must be said that during the last 20 years a considerable number of reactions of the OF radical have been quantitatively investigated [6 - 9]. It is now generally accepted that these radicals, if they have no opportunity to

react with foreign molecules, will disappear in a very fast bimolecular reaction [10 - 12] :



With the exception of the very low pressure region, the wall reaction is insignificant compared with this reaction.

H. J. SCHUMACHER

Universidad Nacional de la Plata, Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Socursal 4 — Casilla de Correo 16 — La Plata (Argentina)

- 1 E. Sanhueza, The chlorine atom sensitized oxidation of CCl_3 , HCF_2Cl and HCF_3 , *J. Photochem.*, 7 (1977) 325.
- 2 E. Sanhueza and J. Heicklen, *J. Phys. Chem.*, 79 (1975) 7.
- 3 H. J. Schumacher and K. Wolff, *Z. Phys. Chem. Abt. B.*, 26 (1934) 453.
- 4 H. J. Schumacher, *An. Asoc. Quím. Argent.*, 194 (1951) 159.
- 5 M. I. López, E. Castellano and H. J. Schumacher, *J. Photochem.* 3, (1974) 97.
- 6 R. Gatti, E. M. Staricco, J. E. Sicre and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, 36 (1963) 211.
- 7 E. R. de Staricco, J. E. Sicre and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, 39 (1963) 337.
- 8 E. Castellano and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, 40 (1964) 51.
- 9 R. Gatti, J. E. Sicre and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, 40 (1964) 127.
- 10 H. G. Wagner, C. Zetsch and J. Warnatz, *Ber. Bunsenges. Phys. Chem.*, 76 (1972) 526.
- 11 J. Czarnowski and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, 86 (1973) 7.
- 12 E. Ghibaudi, J. E. Sicre and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, 90 (1974) 95.

(Received March 10, 1978)