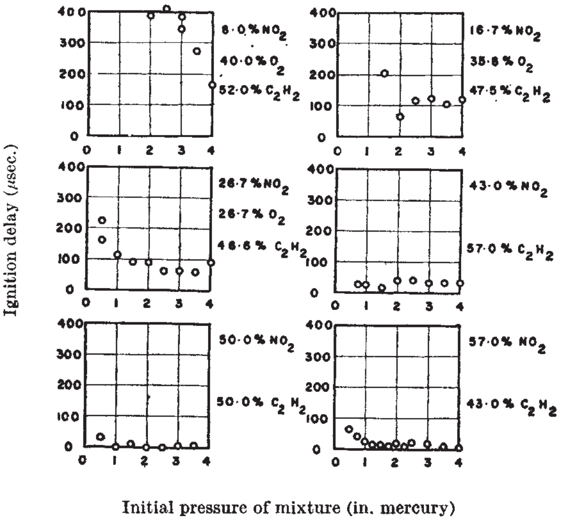

Fig. 2

a measure of the time of the flash with respect to the occurrence of detonation. The time between the first peak in the flash and the occurrence of the extrapolated detonation wave, at the centre of the quartz extension, was arbitrarily taken as the ignition delay.

This ignition delay has been the subject of the early experimentation, and Fig. 2 presents the range of the examination. The variables were the mixture composition and the initial pressure of the mixture. The effect of increasing concentration of nitrogen dioxide was to reduce the ignition delay, while increasing initial pressure had less effect.

In conclusion, stable detonation has been initiated in acetylene, oxygen, nitrogen dioxide mixtures immediately in space, but with a time-delay dependent on mixture composition and initial pressure of the mixture.

J. Wadsworth

Gas Dynamics Laboratory,
Division of Mechanical Engineering,
National Research Council,
Ottawa.

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Radiolysis of Carbon Tetrachloride in the Presence of Oxygen

Carbon tetrachloride containing oxygen from the air is very often used as a solvent for the isolation of radioisotopes, as a radiation–polymerization inhibitor, and as a basic material in chemical dosimetry and in sulphur-35 production as well. Its radiolysis is very significant in all these cases.

When carbon tetrachloride in the presence of oxygen is irradiated, free chlorine, phosgene and hexachlorethane are liberated. This system was investigated by Kailan *et al.*[1–3] many years ago, but their results cannot be interpreted quantitatively. Several authors recently investigated this system in the absence of oxygen and the results obtained by them differ greatly from each other[4–8]. It is impossible to deduce from them the mechanism of radiolysis of carbon tetrachloride in the presence of oxygen. Only Durup[9] occupied himself with the influence of oxygen on radiolysis of carbon tetrachloride, but hitherto nobody has measured the production of phosgene.

We have measured the production of chlorine in carbon tetrachloride irradiated in the presence of oxygen with soft X-rays[10]. Now we present further details about the origin of chlorine and phosgene produced by γ-radiation.

Irradiation was carried out at 22° C. using a cobalt-60 source with a dose-rate of $2\cdot5 \times 10^{16}$ eV./min./ml. carbon tetrachloride. Carbon tetrachloride used was a product of Lachema, grade p.a., dry, without further purification. For the measurement of chlorine the spectrophotometer at wave-length 335 mμ was applied. Phosgene was estimated partly by the colorimetric phenylhydrazine modified method, partly by the acidimetric titration. Doses from a cobalt-60 source were measured by the Fricke ferrous sulphate dosimeter ($G_{\mathrm{Fe}^{3+}} = 15\cdot6$) and a correction on different electron densities was applied.

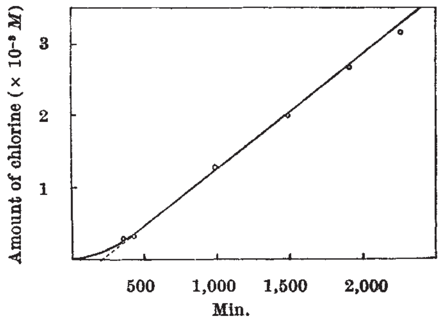

Fig. 1

From Fig. 1 we see that the initial production of chlorine is exponential (induction period up to 140 min. with our conditions) and then linear up to very high doses with $G_{\mathrm{Cl}_2} = 3\cdot6 \pm 0\cdot3$. These results can be explained by the following reactions:

$$\mathrm{CCl_4} \xrightarrow{k_1 I\ \mathrm{CCl_4}} \mathrm{CCl_3} + \mathrm{Cl}$$

$$\mathrm{Cl} + \mathrm{CCl_4} \xrightarrow{k_2} \mathrm{Cl_2} + \mathrm{CCl_3}$$

since the calculated concentration of chlorine has the same graphical shape as the experimental curve, then:

$$[\mathrm{Cl_2}] = k_1 I t - \frac{k_1 I}{k_2\,[\mathrm{CCl_4}]} + \frac{k_1 I\, e^{-k_2\,[\mathrm{CCl_4}]t}}{k_2\,[\mathrm{CCl_4}]} \qquad (1)$$

Through the analysis of the experimental curve from Fig. 1 by the help of equation (1) we then obtain the rate-constants $k_1 I$ and k_2:

$$k_1 I = 2\cdot5 \times 10^{-8} \text{ mole-litre}^{-1} \text{ sec.}^{-1}$$
$$k_2 = 1\cdot1 \times 10^{-5} \text{ mole-litre}^{-1} \text{ sec.}^{-1}$$

The G-value of chlorine is higher than in our earlier work[10], because there we used 30-kV. X-rays and the doses were applied in the induction period range.

In Fig. 2 the amount of phosgene is plotted against the radiation dose. We see that the production of phosgene is linear up to the dose 5×10^{19} eV./ml. with the G-value of phosgene $= 12\cdot1 \pm 1\cdot0$. The situation is rather complicated at high doses and the shape is non-linear. The production of phosgene can be explained by the reactions:

$$CCl_3 + O_2 \xrightarrow{k_3} COCl + Cl_2O$$

$$COCl + CCl_4 \xrightarrow{k_4} COCl_2 + CCl_3$$

$$2\,CCl_3 \xrightarrow{k_5} C_2Cl_6$$

according to which the concentration of phosgene is proportional to the dose :

$$[COCl_2] = \frac{2\,k_1k_3}{k_5}[O_2]\,I^{1/2}t \qquad (2)$$

We are working now on confirming equation (2).

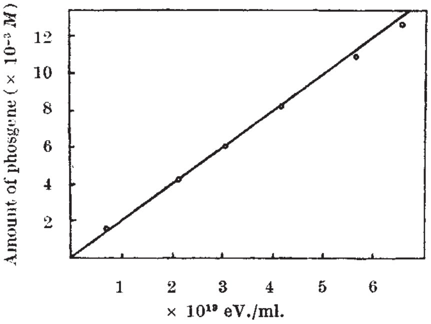

Fig. 2

Both G_{Cl_2} and G_{COCl_2} obtained here are comparable with the results of Durup[9] and other authors[5,7] where $G_{Cl^{\cdot}} = 3{\cdot}9$ and $G_{-O_2} = 8{\cdot}3 \pm 1{\cdot}0$. According to our reactions the value of $G_{Cl^{\cdot}}$ must be the same as G_{Cl_2} and approximately $G_{-O_2} \doteq G_{COCl_2}$. For the time being, we have no explanation for the difference existing between G_{Cl_2} in the absence of oxygen[5-8] and in the presence of oxygen.

We are indebted to Prof. Běhounek for his interest and to our co-workers from the Dosimetric Department of the Nuclear Research Institute for their help.

Zd. Spurný

Nuclear Research Institute,
Na Truhlářce 100, Praha 8.

I. Janovský

Faculty of Technical and
Nuclear Physics,
Praha, Czechoslovakia.

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Liquid Chromatographic Separations using Rubber as the Stationary Phase

In a previous communication[1] it was reported that certain polymers could be separated from mineral oil by a liquid chromatographic method. n-Heptane was used as the mobile phase and small pieces of thin vulcanized natural latex as the stationary phase. It has now been found that compounds of lower molecular weight can also be separated by this method.

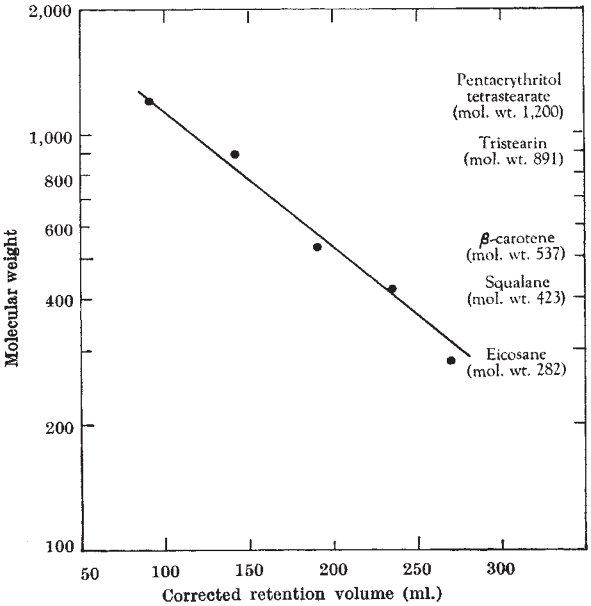

Fig. 1. Effect of molecular weight on corrected retention volume

The use of rubber for the separation of compounds of low molecular weight was first described by Boldingh[2]; he found it advantageous first to swell the rubber with a different solvent from that used as the mobile phase. The use of a cross-linked dextran ('Sephadex') for separating compounds in aqueous solution has been described by Gelotte[3]. Vaughan[4] has mentioned the possibility of using cross-linked polystyrene beads for this purpose.

Boldingh used a fraction of a commercially available rubber powder; but it has been found in these laboratories that columns packed with a similar rubber powder were less efficient than those packed with pieces of surgeons' finger-cots. A column 25 mm.

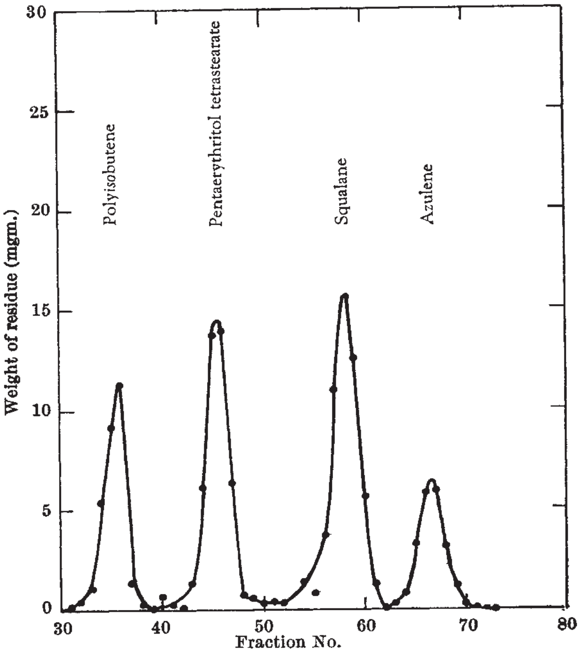

Fig. 2. Separation of a mixture of poly*iso*butene (mol. wt., 18,000), pentaerythritol tetrastearate (mol. wt., 1,200), squalene (mol. wt., 423) and azulene (mol. wt., 128)