

Formation of Polymeric Carbon Suboxide during Gamma Radiolysis of Liquid Carbon Monoxide at 77° K

Buschmann and Groth¹ have reported the formation of carbon dioxide during gamma radiolysis of liquid carbon monoxide at 77° K and have estimated that $G(\text{CO}_2) = 0.18$. These authors detected the formation of a carbonaceous deposit which on heating evolved only small quantities of CO_2 ; they therefore suggested that the deposit was largely composed of solid carbon.

We wish to report experimental data which indicate that the carbonaceous deposit formed during radiolysis of liquid carbon monoxide at 77° K is polymerized carbon suboxide. Furthermore, our results indicate that the reaction stoichiometry in the liquid phase at 77° K is the same as that in the gas phase at 1 atm. and 295° K.

Carbon monoxide, free of oxygen and other impurities, was prepared as described by Clay *et al.*². Irradiations were carried out on a 17,000 Ci source of cobalt-60. Dose rates were determined by ferrous sulphate dosimetry. The silica reaction vessel, about 3 cm³ capacity, had a long fine bore neck (25 cm long, 0.3 cm internal diameter) which terminated on a 'Pyrex' glass vacuum stopcock with a B10 cone-socket connexion. A water cooled jacket, 7 cm long, below the B10 connexion, and an asbestos thermal radiation shield below the water jacket, prevented pyrolysis and oxidation of the tap grease during analysis. Product gases were transferred by means of a single stage diffusion pump and a Toepler pump, to a gas burette. The yields were determined by PVT measurement. CO_2 formed during irradiation was separated from the unreacted CO by passing the contents of the vessel through a spiral trap the lower half of which was refrigerated with liquid oxygen. The solid formed during irradiation was first vacuum pyrolysed at 1,000° C, the CO and CO_2 formed being fractionated in the trap. The carbon remaining after pyrolysis was burnt to CO_2 by adding excess O_2 to the vessel and heating.

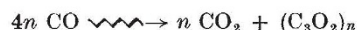
Table 1. GAMMA RADIOLYSIS OF LIQUID CARBON MONOXIDE AT 77° K, ANALYSIS OF REACTION PRODUCTS

Experiment	Total dose (eV × 10 ⁻²⁰)	Radiolytic CO_2 yield (moles × 10 ⁶)	Vacuum pyrolytic analysis of product		Burn off of residual deposit: CO_2 yield (moles × 10 ⁶)
			CO yield (moles × 10 ⁶)	CO_2 yield (moles × 10 ⁶)	
1	2.68	1.11	0.93	0.61	1.95
2	5.10	2.14	1.55	1.06	2.82
3	7.85	3.00	1.81	1.62	4.00
4	21.1	8.15	6.20	4.4	11.3
5	31	11.5	10.0	5.25	14.0

Dose rate, 2.86×10^{17} eV g⁻¹ min⁻¹.

Table 1 shows the result of the analysis. $G(\text{CO}_2)$ estimated from these data is 0.24 ± 0.01 molecules per 100 eV—about 25 per cent higher than that previously reported¹.

If the reaction stoichiometry is



then the C : O ratio for all the reaction products is unity and the C : O ratio for the solid is 1.5. These two ratios calculated from the experimental results are shown in Table 2.

Table 2. GAMMA RADIOLYSIS OF LIQUID CARBON MONOXIDE AT 77° K, MASS BALANCE AND SOLID COMPOSITION RATIOS CALCULATED FROM THE DATA IN TABLE 1

Experiment	$\frac{x}{y}$ on Cx Oy	C in products	
		O in products	O in products
1	1.62	1.05	
2	1.48	0.96	
3	1.43	0.94	
4	1.62	1.10	
5	2.2	0.96	
Average	1.65 ± 0.23	0.96 ± 0.03	

The experimental data indicate that the solid has the composition $(\text{C}_3\text{O}_2)_n$ and that the overall stoichiometry is that discussed here and is identical to that reported by Anderson *et al.*³ for gamma and proton radiolysis of carbon monoxide gas at 1 atm. and 295° K. This result strongly contrasts with the finding of Buschmann and Groth¹, who found that gamma radiolysis of pure liquid CO at 77° K results in the formation of CO_2 and a solid deposit consisting chiefly of carbon. These authors were not able to reconcile this result satisfactorily with the observation that the addition of methane results in the formation of monomeric carbon suboxide. If our results are correct, formation of the solid deposit may be caused by the initial formation of monomeric C_3O_2 and its subsequent polymerization presumably by charge transfer from the primary ion CO^+ . Formation of C_3O_2 monomer on addition of methane can then be explained in terms of competition between C_3O_2 and CH_4 for CO^+ . It is no longer necessary to invoke the formation of two different carbon atom species in the system.

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¹ Buschmann, H. W., and Groth, W., *Z. Naturforsch.*, **22a**, 954 (1967).

² Clay, P. G., Johnson, G. R. A., and Warman, J. M., *Disc. Faraday Soc.*, **36**, 46 (1963).

³ Anderson, A. R., Best, J. V. F., and Willett, M. J., *Trans. Faraday Soc.*, **62**, 595 (1966).

Sorption and Diffusion in Polymers

It has been suggested that the kinetics of water sorption by cellulose as well as the sorption kinetics of other small penetrant molecule-polymer systems in the region where the polymer behaves like a glass can be explained in terms of a coupled diffusion-relaxation mechanism¹⁻³. The sorption kinetics have been studied with the original regenerated cellulose modified by a moderate degree of formaldehyde induced cross-linking.

A series of successive interval sorption measurements on the unmodified cellulose are illustrated in Fig. 1. These curves show the characteristic two-stage sorption, and estimates of the amounts sorbed in each stage are plotted as a function of relative vapour pressure in *A* of Fig. 2. The upper curve is the sorption isotherm of total amount sorbed. The equivalent curves for the treated cellulose are shown in *B* of Fig. 2. The general character of the curves is the same although there are some significant differences between the two samples. The total amount sorbed for the untreated cellulose is greater than that for the treated cellulose and most of this difference seems to result from sorption in the second stage.

The water-cellulose type sorption isotherm is sometimes taken to be due to two "phases" of sorption⁴, and these "phases" seem to correspond to the initial and final stages. The initial stage could correspond to Langmuir⁵ unimolecular layer sorption and the second stage to multimolecular sorption; or the sigmoid shape of the sorption isotherm could be caused by swelling constraint⁶. For polymers at high enough temperatures, at which they behave like rubber, the isotherm corresponds to the Flory-Huggins^{7,8} theory, and this type of isotherm seems similar to the second stage curve of Fig. 2.

It would seem that the sorption isotherms and the anomalous kinetic behaviour in the glassy state are re-