contraction. The extreme entropy loss in the didiol type complex formation can be ascirbed to the fact that the present ligands are the OH groups on the polymeric PVA chain: the PVA chain must take a special conformation favourable to react with the tetrahedral borate ion, i.e., two sets of adjacent OH groups of PVA must be in a *cis*-conformation[9-16]. Furthermore, crosslinking might be expected to cause considerable reduction in the conformational entropy of the PVA chain. Thus, it appears that here, as in the other polyol–borate systems, the main contribution to the complex stabilities for the present PVA–borate complexes are the favourable enthalpy changes, in contrast to most metal complexes where the complexing ability results mainly from the entropy contribution[17].

Finally, since the present PVA–borate complexes are both polyelectrolytes, the effect of ionic strength must be taken into consideration and the values are not always definitive. But, the present results are felt to be valid as a first stoichiometric approach for the thickening and gelling phenomena of aqueous PVA–borax system.

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A commentary on 'Free radicals and new end groups resulting from chain scission: 1. γ-Irradiation of polyethylene'

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Introduction

Under the above title DeVries, Smith and Fanconi[1] (DSF) recently published a paper in which they have attempted to relate the concentration of free radicals produced in the γ-irradiation of polyethylene (PE) to 'the resultant concentration of new chemical groups'. However, their estimates of free radical yields differ from commonly accepted values by an order of magnitude. Furthermore as explained below they overlooked what is probably the most important mechanism for the formation of *t*-vinylene double bonds. Let us consider the free radical yield problem first.

Free radical yields. Using a linear polyethylene DSF irradiated a sample *in vacuo* at 77K to a dose of 50 Mrad and measured the free radical yield by the e.s.r. method at −160°C. From the data of their *Figure 3* and of *Tables 2* and *3* it is possible to calculate $G(\mathrm{R}\cdot)$ or the number of free radicals produced per 100 e.V. of absorbed radiation from the equation

$$G(\mathrm{R}\cdot)=\frac{[\mathrm{R}\cdot]100}{r} \qquad (1)$$

where r is the dose in e.V. g^{-1} that produced a concentration $[\mathrm{R}\cdot]$ of free radicals per gram. Since[2] 1 rad equals 6.25×10^{13} e.V., 50 Mrad is 31.25×10^{20} e.V. and since $[\mathrm{R}\cdot]$ was found by DSF to be 4.8×10^{18} radicals per gram for their irradiation in vacuum, $G(\mathrm{R}\cdot)$ can be calculated to be only 0.15. For their 3 Mrad irradiation *in vacuo*, $G(\mathrm{R}\cdot)$ is calculated to be 0.21. Dole[3] has summarized $G(\mathrm{R}\cdot)$ values obtained by a number of workers; for Marlex-6002 irradiated to 20 Mrad at 77K values range from 3.6 for films to 4.2 for single crystals. More recently[4] for a 7 Mrad dose at 77K Gvozdic and Dole found $G(\mathrm{R}\cdot)$ equal to 2.96 (average of 4 samples) for annealed Marlex-6002 (PE) and 3.59 (average of 6 samples) for the quenched samples. Waterman and Dole[5] showed that for radiations in vacuum (they used electron beam irradiation) at 77K the alkyl free radical yield was constant with dose up to 70 Mrad. Their $G(\mathrm{R}\cdot)$ value was 3.3 ± 0.5 which demonstrates no essential difference between γ-ray and electron beam irradiation of the 10 mil thick Marlex-6002 film used by them. DSF's yield of free radicals was also constant with dose for their vacuum irradiations.

All of the above mentioned $G(\mathrm{R}\cdot)$ values are an order of magnitude greater than those calculated from DSF's data. The exact cause of this discrepancy is unknown at the present time. DSF did not describe how they calibrated the dose of γ-rays absorbed by their samples. They used 1.25 mW power in their e.s.r. measurements whereas we[4] have found that alkyl radicals saturate at a power of 0.063 mW.

Double bond yields. DSF give 5.4 ± 3.5 and 2.3 ± 1 for their yields of *t*-vinylene double bonds per free radical for doses of 3 and 50 Mrad *in vacuo* at 77K respectively. Multiplying these numbers by the $G(\mathrm{R}\cdot)$ values calculated

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by us from their data, we find $G(t\text{-Vl})$ equal to 1.13 and 0.50. Waterman and Dole[6] studied the growth of the infrared absorbance at 966 cm^{-1} as a function of dose and found that their yields, in contrast to DSF's yields, were independent of dose up to 200 Mrad. Waterman and Dole irradiated their PE films at 77K *in vacuo* and measured the i.r. absorbance at room temperature. They also measured it at 77K and then after heating to room temperature in a separate experiment and found that for a dose of 35 Mrad the absorbance increased slightly from 0.241 to 0.254 during the heating process. Waterman and Dole's $G(t\text{-Vl})$ was 1.03 for the 77K irradiation which agrees within 10 per cent with DSF's value given above for their low dose experiment. For irradiations at room temperature Kang *et al.*[8] found $G(t\text{-Vl})$ equal to 2.4 if the data were extrapolated to zero dose but equal to 1.4 for a dose of 27 Mrad. The reduction in yield between zero and 27 Mrad was partly the result of the radiation induced crosslinking reaction involving the double bonds, and partly the reduction in hydrogen evolution. At 120° the reduction in $G(t\text{-V1})$ between 0 and 27 Mrad dose could be explained entirely in terms of the increase in the G-value for crosslinking, $G(\mathrm{X})$. It is interesting to point out that as discovered many years ago by Dole *et al.*[7] the growth of the t-V1 group for irradition accurately follows the equation

$$[t-\mathrm{V1}]-[t-\mathrm{V1}]_0=\frac{\varphi_0}{k_1}(1-\mathrm{e}^{-k_1 r}) \tag{2}$$

where φ_0 is the zero order growth constant, k_1 is the first order decay constant and $[t-\mathrm{Vl}]_0$ is the t-vinylene concentration at zero dose. For very small values of $k_1\,r$ equation (2) reduces to

$$[t-\mathrm{Vl}]-[t-\mathrm{Vl}]_0=\varphi_0 r \tag{3}$$

which is applicable to the data obtained at 77K.

Inasmuch as considerable double bonds are produced during irradiations at 77K where free radicals are frozen in and cannot react it is clear that the chief mechanism of double bond formation is not one involving the recombination of free radicals. Instead the major reaction producing the t-vinylene group is the exothermic process.

$$-\mathrm{CH_2}-\overset{+}{\mathrm{C}\mathrm{H}}_2- \rightarrow \mathrm{H_2} + -\mathrm{CH}=\overset{+}{\mathrm{C}\mathrm{H}}- \tag{4}$$

which DSF did not take into consideration. Our ratio of double bonds to free radicals for irradiations at 77K was 0.31 (constant with dose) in contrast to DSF's estimates varying from 2.3 to 5.4 (vacuum irradiations).

Crosslink yields. DSF did not measure crosslink yields themselves, but they did state that $G(\mathrm{X})$ was equal to or slightly higher than the value for carbon carbon double bond formation. In the work of Kang *et al.*[8] mentioned above, it was found that the $G(\mathrm{X})/G(t\text{-Vl})$ ratio when extrapolated to zero dose was only 0.42 for irradiations at 37°C and 0.45 for irradiations at 120°C. As the dose increased to 27 Mrad and the irradiation caused the disappearance of the double bonds, the ratios rose to 1.07 and 1.64 at 35°C and 120°C respectively. Hence the relative yields of crosslinks and double bonds depend on the temperature of the irradiation and the magnitude of the dose.

Carbonyl group formation. DSF found that 11 ± 4 $\mathrm{C=O}$ groups were produced per free radical for irradiations in a vacuum, their *Table 2*. It is hard to understand why any carbonyl groups at all should have been formed in an evacuated system. Probably the oxygen atoms were picked up by exposure of the irradiated film to air before the i.r. measurements were made.

When PE is irradiated, allyl free radicals, $-\mathrm{CH_2\dot{C}H=CH_2}$ and $-\mathrm{CH_2\dot{C}HCH=CH_2}$, are formed as well as alkyl free radicals, $-\mathrm{CH_2\dot{C}HCH_2}-$. The allyl free radicals are relatively stable at room temperature and the PE must be heated to 90°C in some highly crystalline samples before appreciable decay occurs[9]. In Marlex type PE as used by DSF the allyl radicals are so stable at room temperature that they will react with oxygen of the air to form carbonyl groups for as long as 2 months after the irradiation[10]. Apparently DSF did not take this into account.

Conclusion

Our conclusion is that the paper[1] of DSF should be re-evaluated in the light of the above comments.

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