Effects of Scavengers on the Radiolytic Formation of Buta-1,3-diene from *trans*-But-2-ene in Dilute Gaseous Mixtures

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IN radiation chemistry, *trans*-but-2-ene has been used[1] to detect methylene radicals formed from CH_4 and studies have been carried out of hydrogen formation[2] and of overall product formation[3] from the γ-irradiated unsaturate. In the latter work,[3] buta-1,3-diene was not listed as a product from either the liquid or the gaseous butene.

We have now found that buta-1,3-diene is produced in irradiated pure gaseous but-2-ene ($G = 0{\cdot}13$) and in its mixtures with Ar or CH_4. In addition, its yield is markedly increased by small additions of N_2O and reduced to zero by small additions of SF_6, both these additives being generally used in radiation chemical studies as electron scavengers.

Mixtures of about 10 mole % *trans*-but-2-ene in Ar or CH_4 in 1·9-l. silica vessels were irradiated with ^{60}Co γ-rays at dose rates of 2·0 and $1{\cdot}5 \times 10^{19}$ ev l.$^{-1}$ hr.$^{-1}$ respectively. The total gas pressure was about 107 kN m.$^{-2}$ and the irradiation temperature was about 30°. In scavenging experiments 1·1 kN m.$^{-2}$ SF_6 or 4 kN m.$^{-2}$ N_2O were added. Analyses were performed by g.l.c. with an 8-m. dimethylsulpholan column at 0° and then on a 1·3-m. $AgNO_3$ column at 20°.

On the assumption that $G = 10$ for but-2-ene disappearance, about 0·5% would be destroyed at the maximum doses given. This calculation excludes geometrical isomerisation, which is extremely rapid[4] in the presence of SF_6. The destruction of butadiene during the irradiation would also be minimal owing to its low concentration, the presence of a large excess of but-2-ene acting as a protector, and the relatively low G-value for butadiene destruction (which was found to be about 18 in mixtures of 0·1% C_4H_6 in Ar, independent of the presence or absence of N_2O or SF_6).

G-Values for butadiene formation from trans-but-2-ene

	Mixture	
Scavenger	CH_4–C_4H_8	Ar–C_4H_8
None	0·20	0·42
N_2O	3·5	0·44
SF_6	0·00	0·00

The results are shown in the Figure, from which the initial G-values given in the Table were calculated. It appears that N_2O has no effect on the initial butadiene yield in Ar, but has a pronounced accelerating effect in CH_4, whereas SF_6, which is a more effective scavenger, completely suppresses the formation of butadiene.

The addition of about 1·3 kN m.$^{-2}$ of NH_3, NMe_3, NO, and O_2 had little effect on the budadiene yield compared with the effects of N_2O and SF_6, so that radical reactions and positive ion–molecule reactions appear to be unimportant in this instance.

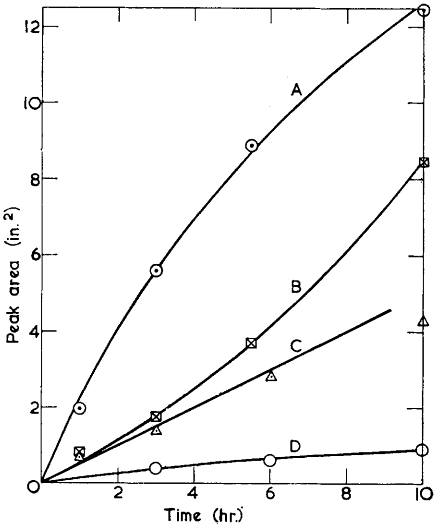

FIGURE. *Yield of buta-*1,3-*diene as a function of irradiation time.* A: CH_4–C_4H_8–N_2O; B: Ar–C_4H_8–N_2O; C: Ar–C_4H_8; D: CH_4–C_4H_8.

The results will be discussed on the basis of the assumption that an important mode of butadiene formation is the neutralisation of the but-2-ene parent ion by a thermal electron:

$$C_4H_8^+ + e^- \longrightarrow C_4H_6 + 2H \qquad (1)$$

In the presence of SF_6 reaction (1) is suppressed and the but-2-ene ions are neutralised by other negative species (such as SF_6^-) in reactions permitting extensive energy partition.

Since N_2O is also an efficient electron scavenger it can also be assumed to prevent electron neutralisation of the butene parent ion. However, the

N_2O^- formed is known to dissociate to give O^-, and Warman[5] has suggested the sequence

$$O^- + C_4H_8 \longrightarrow C_4H_7^- + OH \qquad (2)$$

$$C_4H_7^- + N_2O \longrightarrow C_4H_6 + N_2 + OH^- \qquad (3)$$

as a possible explanation of enhanced N_2 yields in certain irradiated alkene–N_2O systems. Thus butadiene may be formed despite the removal of electrons by N_2O. In the Ar–N_2O system, O^- will react with N_2O as well as with C_4H_8,

$$N_2O + O^- \longrightarrow N_2 + O_2^- \qquad (4)$$

$$N_2O + O^- \longrightarrow NO + NO^- \qquad (5)$$

with $k_4/k_2 = 5$ and $k_5/k_2 = 3{\cdot}7$ (*cf.* Table II, ref. 5). In the present experiments $[N_2O]$ $[C_4H_8]$ $= 0{\cdot}38$, so that $(R_4 + R_5)/R_2 = 3{\cdot}3$ and only $\frac{1}{4}$ of the O^- can react to form $C_4H_7^-$. If the ion-pair yield in Ar is taken as 4, and if all electrons are scavenged by N_2O, the maximum value of $G(O^-)$ is 4 and hence $G(C_4H_7^-)_{\max} = 1$. Since $G(C_4H_6)$ $= 0{\cdot}44$ in the presence of N_2O, reaction (3) appears to be nearly 50% efficient. This is remarkably high. Furthermore, in the CH_4–N_2O system $G(C_4H_6) = 4\,G(C_4H_7^-)$ and some other source of butadiene involving the participation of CH_4 in the reaction scheme is indicated. It can be shown that the reaction

$$O^- + CH_4 \longrightarrow OH^- + CH_3 \qquad (6)$$

is almost certainly exothermic whereas (2) is probably slightly endothermic or thermoneutral. Consequently the conversion of O^- into OH^- *via* reaction (6), followed by the exothermic reaction

$$OH^- + C_4H_8 \longrightarrow C_4H_7^- + H_2O \qquad (7)$$

sets up a chain sequence between (7) and (3) more readily when CH_4 is present than when it is absent. The probable competition set up owing to occurrence of the analogous reaction between OH^- and CH_4,

$$OH^- + CH_4 \longrightarrow CH_3^- + H_2O \qquad (8)$$

may be compensated by generation of $C_4H_7^-$ *via* the proton transfer reaction

$$CH_3^- + C_4H_8 \longrightarrow C_4H_7^- + CH_4 \qquad (9)$$

For (9) to be exothermic, the heat of formation of $C_4H_7^-$ must be less than 14 kcal./mole if $\Delta H_f(CH_3^-) = 7$ kcal./mole.[6] These values fit well into thermocycles based on the reactions (2), (6), (7), and (8) if the electron affinities of CH_3 and C_4H_7 are taken as 26 (*cf.* ref. 7) and 13 kcal./mole, respectively. The latter agrees well with the trend of values for other hydrocarbon molecules and radicals as compiled and tabulated recently by Freeman[8] [who also cites evidence for a reaction between OH^- and methylcyclohexane analogous to (7)].

It appears that a plausible reaction scheme involving negative hydrocarbon ions can account for these effects produced by N_2O and SF_6 in this system.

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