Ionic Processes in the Radiolysis of Nitrous Oxide

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Summary The addition of small amounts of sulphur hexafluoride to nitrous oxide before irradiation reduces the nitrogen yield by an amount which indicates that more than one nitrogen molecule is produced for each electron arising from the ionisation of the nitrous oxide.

RECENTLY,[1] the effect of small additions of SF_6 on the G-value for N_2-formation from gaseous N_2O was reported; $G(N_2)$ was reduced from 10·1 in pure N_2O to 8·0 in the presence of 0·01—0·3% SF_6. This observation was used in reaching the conclusion that one electron produces one, or less than one, molecule of N_2, and hence that the mechanism

$$e^- + N_2O \rightarrow N_2 + O^- \qquad (1)$$

$$O^- + N_2O \begin{cases} \nearrow N_2 + O_2^- & (2) \\ \searrow NO + NO^- & (3) \end{cases}$$

cannot apply since it implies that more than one N_2 molecule should be produced per electron.

We were not aware of the work of Takao, *et al.* when, during a study[2,3] of the effects of N_2O and SF_6 on *cis-trans* isomerisation reactions, a few experiments were carried out to determine the effect of small amounts of SF_6 on $G(N_2)$ from irradiated N_2O at temperatures from 30 to 200°. The results obtained, however, are sufficiently different from that cited to cast some doubt on the conclusion that one, or less than one, N_2 molecule is formed per electron.

The irradiations were carried out in a 1·9 l. silica vessel at a pressure of 80 cm. Hg (at 20°). The γ-ray dose rate was about 2×10^{19} ev $l.^{-1}hr.^{-1}$. At each temperature a set of irradiations of 3—20 hr. duration was used to construct yield–time curves for N_2 from which initial rates could be estimated. Gas chromatography was used for the analyses.

The initial rates, converted to G-values by assuming $G(N_2) = 11{\cdot}0$ from pure N_2O at near-ambient temperatures,[4] are shown in the Figure as a function of temperature and SF_6 content. At 30°, $G(N_2)$ is reduced from 11·0 to 7·2, or 3·8 G units, by the addition of 1·0 vol. % SF_6. With increasing temperature $G(N_2)$ from pure N_2O rises smoothly, in reasonably good agreement with the findings of Jones and Sworski[5] (but not with those of Gorden and Ausloos[6]), while the residual $G(N_2)$ in the presence of 1% SF_6 rises only very slowly. With 0·1% SF_6 the N_2 yield is slightly lower and invariant with temperature; it appears possible that an excess of SF_6 can contribute to N_2-formation in some way.

On the assumption that SF_6 acts only as an electron scavenger, the change in $G(N_2)$ of 3·8 units at 30°, taken in conjunction with $W(N_2O) = 33{\cdot}0$, gives $G(e^-) = 3{\cdot}0$ and indicates that about 1·3 N_2 molecules are produced for each electron arising from the ionisation of N_2O. This means that reactions (1)—(3) can in fact account for the ionic contribution to N_2-formation at that temperature. Since the curves in the Figure appear to be approaching limiting values at the lowest temperature, it may be valid to compare the present results with those of Robinson and Freeman,[7] obtained at −88° with pure N_2O. On the basis of their results a mechanism was suggested which included reactions (1)—(3) and yielded $G(N_2) = 3{\cdot}5$ as the sum of (1) and (2). The agreement of this conclusion with the present work gives substance to the view that reactions (1) and (2), or equivalent reactions involving N_2O^-, do occur during the radiolysis of N_2O.

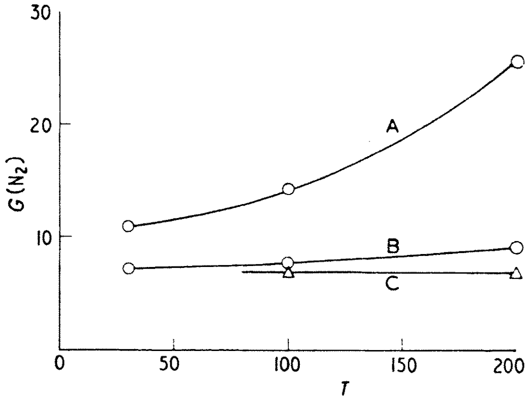

FIGURE. *Variation of* $G(N_2)$ *with temperature and the effect of added* SF_6; A: *Pure* N_2O; B: N_2O + 1 *vol.* % SF_6; C: N_2O + 0·1 *vol.* % SF_6.

The relative constancy of $G(N_2)$ with rising temperature in the presence of SF_6 is evidence that most of this N_2 is produced by reactions such as $N_2O^* \longrightarrow N_2 + O$, which require no activation energy acquired by collisions with other molecules. On the other hand, the ionic processes inhibited by SF_6 obviously require some activation energy; these will be processes subsequent to reactions (1)—(3) or their equivalents, which we assume from the apparent attainment of a limiting value for $G(N_2)$ at low temperatures require no activation energy. Gorden and Ausloos[6] suggested the reactions

$$NO^- + N_2O \rightarrow NO + N_2 + O^- \qquad (4)$$

$$O_2^- + N_2O \rightarrow O_2 + N_2 + O^- \qquad (5)$$

their measurements indicating that (4) is more probable. As they pointed out, these reactions regenerate O^- and thus can account for the temperature effects which they, by isotopic analyses, and we, by the use of SF_6, have observed.

The present results seem to agree well with the mechanistic implications of the work of Freeman[7] and Ausloos,[6] rather than with those of Takao.[1] It is possible that the total dose ($7{\cdot}2 \times 10^{20}$ ev $g.^{-1}$) given in the latter work was excessive; it has been shown[4,8] that the N_2 yield is no longer linear with dose above 3—6 $\times 10^{20}$ ev $g.^{-1}$. At higher doses $G(N_2)$ from pure N_2O would tend to be low, whereas in the presence of SF_6 the accumulation of N_2, which is formed mainly from N_2O^*, would probably still be linear with dose. The difference would thus be incorrectly low.

A very recent Note by Sears[9] reports a reduction in $G(N_2)$ of 3·2 ± 0·5 by the electron scavengers SF_6, NO_2, and CCl_4 and casts doubt on the importance of reaction (2). However, from his tabulated results it would seem reasonable to take weighted averages of $G(N_2)$ for γ-irradiated pure N_2O in the gas phase at densities up to 0·10 g. cm.$^{-1}$ and for all his results with N_2O at 800 torr containing varying amounts of SF_6, NO_2, and CCl_4. This calculation yields $\Delta G(N_2) = 10{\cdot}6 - 7{\cdot}1 = 3{\cdot}5$ and thus provides support for the present contention that reaction (2), or its equivalent, is important in the radiolysis of N_2O.

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