character would in turn be expected to enhance the rate of intramolecular reaction to give fluoranthene.

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## Radiolysis of Nitrous Oxide in the Adsorbed State[1]

*Sir:*

The radiolysis of molecules physically adsorbed on solids often results in such large decomposition compared to that in the liquid and gaseous states that energy directly absorbed by the solid must be transferred to the sorbate.[2-7] This apparent energy-transfer phenomenon is incompletely understood at present. Nitrous oxide is a well-known electron scavenger, and one of its decomposition products, nitrogen, is unlikely to chemisorb on the sorbent surface. Results on the radiolysis of $N_2O$ adsorbed on silica gel[8] at 10° are reported here. Experimental methods have been described elsewhere.[9]

Experiments in which $N_2O$ adsorbed on unirradiated and irradiated sorbent (dose, $40 \times 10^6$ rads) resulted in negligible $N_2O$ decomposition compared to that when sorbent and $N_2O$ were irradiated together. The products measured were $N_2$ and $O_2$, and in three series of experiments in which dose, surface $N_2O$ concentration, and surface hydroxyl concentration were varied, the nitrogen to oxygen ratios found were $2.0 \pm 0.1$, $2.3 \pm 0.3$, and $1.9 \pm 0.1$. The stoichiometry of the decomposition is apparently

$$N_2O \longrightarrow N_2 + 0.5O_2$$

In all experiments, $97 \pm 2\%$ of the nitrogen desorbed at room temperature while, depending on the experiment, some 50–90% of the total amount of oxygen was observed. The remaining oxygen could only be recovered by degassing at 450° and was apparently chemisorbed on the surface. The greater the total amount of oxygen the smaller was the fraction retained on the surface at room temperature. No hydrogen was detected in the radiolysis products.

At constant surface coverage or electron fraction of $N_2O$, $G(N_2)$ was independent of dose up to 25 Mrads but decreased with further increase in dose. At a constant dose of 19 Mrads, $G(N_2)$ increased with electron fraction and appeared to be approaching a constant value at about 0.05 electron fraction (Figure 1). The $G(N_2)$ values observed (0.52 at electron fraction 0.0004 to 3.1 at 0.05) are so high that efficient energy transfer from the solid to the adsorbed $N_2O$ must be taking place.

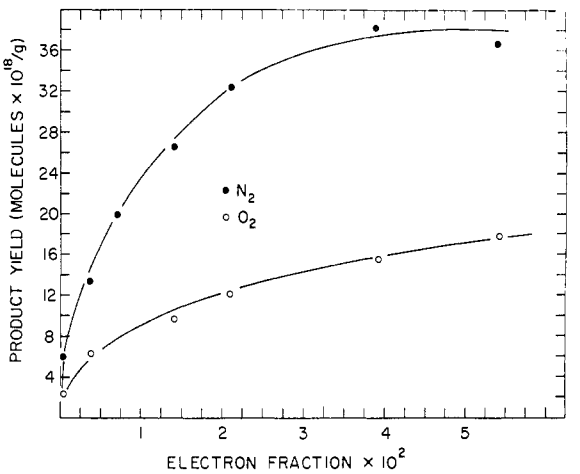


Figure 1. Formation of $N_2$ and $O_2$ as a function of electron fraction of $N_2O$ adsorbed on silica gel (dose, $19 \times 10^6$ rads).

The results in Figure 1 can be explained by invoking electrons as energy-transfer carriers. Electrons formed in the bulk solid migrate rapidly to the surface where they either react with $N_2O$ or become trapped. The $O^-$ and trapped electrons then react with the positive holes (+) (eq 1–4). Volume trapping of electrons or positive holes in the bulk sorbent is considered to be negligible, since for this particular gel they will always be within 11 Å of the surface.

$$e^- + (N_2O)_S \longrightarrow N_2 + (O^-)_S \quad (1)$$

$$e^- + \text{surface} \longrightarrow (e^-)_S \quad (2)$$

$$\oplus + (e^-)_S \longrightarrow \text{energy} \quad (3)$$

$$\oplus + (O^-)_S \longrightarrow (O)_S \quad (4)$$

This mechanism leads to the relationship

$$G(N_2) = \frac{G_e\text{-}k_1\theta}{k_1\theta + k_2(1 - \theta)} \quad (5)$$

where $\theta$ = surface coverage of $N_2O$ = $(v)_S/v_m$ = (amount of $N_2O$ sorbed)/(amount of $N_2O$ at monolayer coverage). Rearrangement of eq 5 gives

$$\frac{k_1 - k_2}{k_1 G_e\text{-}} + \frac{k_2 v_m}{k_1 G_e\text{-}(v_{N_2O})_S} = \frac{1}{G(N_2)} \quad (6)$$

and a plot of $1/G(N_2)$ *vs.* $1/(v_{N_2O})_S$ or $1/N_2$ *vs.* $1/(v_{N_2O})_S$ should be linear as is found in Figure 2 in the range $\theta$ = 0.01–0.20. From the slope and intercept and taking 17 Å$^2$ for the area of the $N_2O$ molecule, $G_e\text{-} = 3.7$ and $k_2/k_1 = 2.9 \times 10^{-2}$.

If the electrons are assumed to be first trapped on the surface, before reacting with $N_2O$ or positive holes, eq 7, similar to eq 6, results, where $k_2' = k_1[\oplus]$, and concentrations are expressed per unit area of solid. $G_e\text{-}$ is then 3.9 and $k_2'/k_1 = 215$ μmoles/g = 0.28 μmole/m$^2$. This mechanism predicts that $G(N_2)$ is dependent on dose rate. In preliminary experiments $G(N_2)$ has

$$\frac{1}{G_e\text{-}} + \frac{1}{G_e\text{-}}\frac{k_2'}{k_1(N_2O)_S} = \frac{1}{G(N_2)} \quad (7)$$

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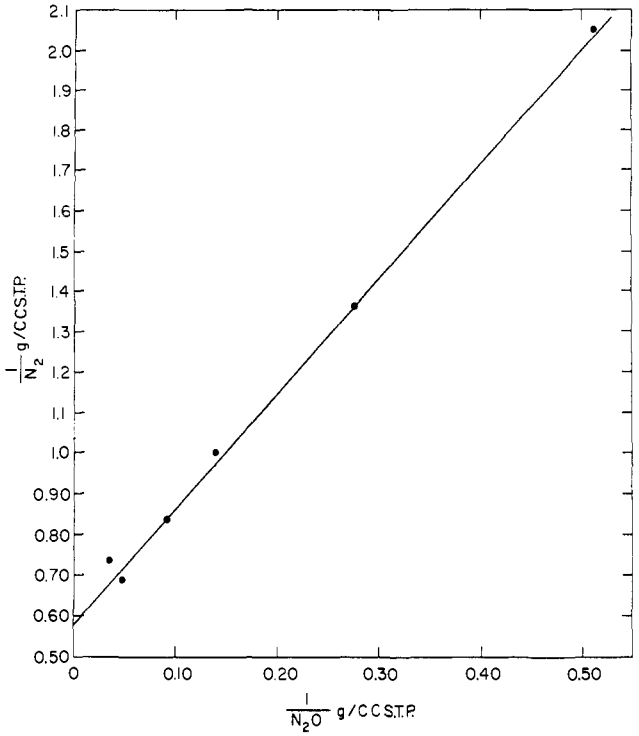


Figure 2. Data of Figure 1 plotted according to eq 6.

been found to be independent of intensity in the range $6.6 \times 10^2$ to $9.8 \times 10^6$ rads/hr.

It is possible that the additional reactions

$$(O^-) +_S [N_2O]_S \longrightarrow [O_2^-]_S + N_2 \quad (8)$$

$$[O_2^-]_S + \oplus \longrightarrow O_2 \quad (9)$$

are occurring. Our present results suggest that reaction 8 is either absent or very fast in which case $G_e = 1.35$, $k_2/k_1 = 1.5 \times 10^{-2}$, and $k_2'/k_1 = 0.14$ $\mu$mole/m$^2$.

The apparent energy transfer can be equally well explained by migration of excitons which either react with adsorbed $N_2O$ or are annihilated by the surface. At the moment, the electron hypothesis is preferred because $N_2O$ is known to be an electron scavenger in the liquid and gas phases. Also an electron-transfer mechanism has been proposed to explain the catalytic decomposition of $N_2O$ on semiconductor surfaces.[10]

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## The Dehydrotetracyclines. I. Epimerization at C-6

*Sir:*

In 1958 McCormick and co-workers[1] reported the isolation of 7-chloro-5a(11a)-dehydrotetracycline (I) which was accumulated by *Streptomyces aureofaciens* Duggar mutant S-1308, descended from the original 7-chlorotetracycline-producing A-377 soil isolate of Duggar. Its structure was established by spectral and elemental analysis as well as by catalytic reduction to an equimolar mixture of tetracycline and 5a-epitetracycline. Biological reduction[2,3] gave only 7-chlorotetracycline, thus showing conclusively[2] that I is a precursor of 7-chlorotetracycline and that the last step in 7-chlorotetracycline biosynthesis is the stereospecific reduction of the double bond. Miller and co-workers[4] have shown that 5a(11a)-dehydrotetracycline is the common intermediate for the biosynthesis of tetracycline and oxytetracycline and Mitscher and co-workers[5] have used this study to biologically hydroxylate and reduce I to give 7-chloro-5-hydroxytetracycline. Photooxidation of anhydrochlorotetracycline gives the 6-hydroperoxide of I.[6]

The position of the double bond in I has been the subject of some discussion,[6,7] and two tautomers have been isolated.[7] However, the only reported reactions involving I (besides reduction) are acid-catalyzed rearrangements with water[8] and alcohols[7] to give 5-hydroxy- or alkoxyanhydrotetracyclines.

We have now found that I undergoes stereospecific inversion at C-6 in liquid hydrogen fluoride containing 2 equiv of $H_2O$ to give 7-chloro-6-epi-5a(11a)-dehydrotetracycline (II) in 20–25% yield; $[\alpha]^{25}D$ +40.5 ± 6° (*c* 0.493, 0.1 *N* HCl); $\lambda_{max}^{KBr}$ 5.85 $\mu$; $\lambda_{max}^{0.1\ N\ HCl}$ 253, 319, 385 m$\mu$ (log $\epsilon$ 4.43, 3.79, 3.99); $\lambda_{max}^{0.1\ N\ NaOH}$ 243, 341, 419 m$\mu$ (log $\epsilon$ 4.31, 3.88, 3.88).

*Anal.* Calcd for $C_{22}H_{21}N_2O_8Cl \cdot 0.5H_2O$: C, 54.38; H, 4.56; N, 5.77; Cl, 7.30; $H_2O$, 1.9; mol wt, 476.-0985. Found: C, 54.69; H, 4.66; N, 5.24; Cl, 7.15; $H_2O$, 2.1 (glpc); mol wt (mass spectroscopy), 476.0989).

Although the ultraviolet and infrared spectra of II are very similar to those of I, the nmr spectrum clearly is distinct. Whereas the C-methyl absorption of I in deuteriodimethyl sulfoxide is at 109 Hz, the absorption of II is at 85 Hz (both are unsplit singlets). This observation is in agreement with that of Schach von Wittenau and Blackwood[9] wherein the absorption of the C-6 methyl group in $\beta$-6-deoxyoxytetracycline is 42 Hz upfield from that of the $\alpha$-6-deoxy derivative. In these latter cases inversion of a C-6 methyl group in tetracycline or oxytetracycline has taken place upon catalytic hydrogenolysis of the C-6 hydroxyl to give the C-6 $\beta$ methyl group.[10]

Final proof of the structure of II involved catalytic hydrogenation to give 6-epitetracycline (III) and 5a-epi-6-epitetracycline (IV), both of which were converted to 5a(6)-anhydrotetracycline (Va). 6-Epitetracycline (III) [$[\alpha]^{25}D$ −100 ± 6° (*c* 0.448, 0.1 *N* HCl); $\lambda_{max}^{0.1\ N\ HCl}$ 268, 349 m$\mu$ (log $\epsilon$ 4.17, 4.07); $\lambda_{max}^{0.1\ N\ NaOH}$ 250 (sh) (log

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