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Free Radicals Produced by γ Irradiation of Nitroalkanes in Frozen Glassy Acidic Solutions

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The scavenging of paramagnetic species by nitroalkanes formed during the γ irradiation of aqueous 6.4 molar sulfuric acid glasses has been studied by using ESR. Nitroalkanes give rise to RNO_2H radiclas, the nitrogen hyperfine coupling of which has the values $A_{//}^{N}=48$ G and $A_{\perp}^{N}=18$ G with $g_{//}=2.0035$ and $g_{\perp}=2.0075$. The RNO_2H yields for 0.5 molar solutions of nitromethane and 2-nitro-2-methyl-propanol are $G\simeq4$ and $G\simeq3$, respectively. $G(SO_4^-+OH^\cdot)$ is roughly idenpendent of the nitroalkane concentration. These results are interpreted as the scavenging of hydrogen atoms due to the energetic recombination of non-hydrated primary species (H_2O^+, $OH^\cdot$, e^-) according to an assumption of Hamill.

Since the first report by Livingston[1] of the possibility of trapping hydrogen atoms in glassy acidic matrices below 100 K, several ESR investigations have been made on the mechanism of formation, the spatial distribution and the thermal decay of trapped hydrogen atoms.[2] Only a few studies have been devoted to the radicals formed in the presence of electron and hydrogen atom scavengers. Among these radicals, the nitroalkanes are known to be particularly efficient as shown by ESR[3-6] and optical absorption studies[7,8] on liquid solutions of these compounds in polar solvents or in water.

The present work was carried out to identify the radicals from γ irradiated nitroalkanes at low temperature in glassy sulfuric acid aqueous solutions and to investigate their formation mechanism. The results of this study will be compared to those of a previous one in which nitroalkanes were irradiated in concentrated alkaline aqueous solutions[6] giving rise to unexpectedly high radical yields.

Experimental

Nitromethane (NM) was distilled at 72—74°C at pressure of 400 Torr in an argon atmosphere through a column containing a rotating helicoidal band. 2-Nitro-2-methyl-propanol (NMP) furnished by Aldrich Chemicals was used without further purification. Acidic solutions of nitroalkane were prepared just before degassing under vacuum. They were plunged into liquid nitrogen resulting in clear transparent glasses and stored at 77 K until they were irradiated. The irradiation dose rates were determined by ferrous sulfate dosimetry of the ^{60}Co source taking $G(Fe^{3+})=15.5$. The usual dose rates were 5.8×10^{19} eV mol^{-1} h^{-1} and 1.67×10^{20} eV ml^{-1} h^{-1}.

The ESR spectra were recorded with a Strand Labs 601 BX spectrometer operating at 9250 MHz with a 10 kHz field modulation. The microwave power level was kept below 0.1 mW to prevent saturation of the signals. The absolute yield of radicals trapped in the acidic matrix at 77 K was determined by double integration of the ESR spectra using $G(e_s^-+CH_3CHOH)=8$ for the reference sample of glassy ethanol irradiated under the same conditions and 1.3 for the ratio of the absorbed irradiation doses in 6.4 molar sulfuric acid glass and in ethanol.

The ESR experiments were completed by subsidiary gas chromatographic measurements of the molecular hydrogen yield by the method reported in Ref. 9.

Results and Discussion

Identification of the Free Radicals. *Glassy Aqueous Solutions of H_2SO_4 without Additives*: The ESR spectrum of γ irradiated H_2SO_4/H_2O glass consists of an asymmetrical singlet centered in the vicinity of $g=2.01$ and two lines separated by 505 G corresponding to trapped hydrogen atoms as shown in Fig. 1a. The singlet is attributed to either $SO_4^{\cdot-}$ or $HSO_4^{\cdot}$ radicals, but are hard to distinguished on account of the absence of hyperfine

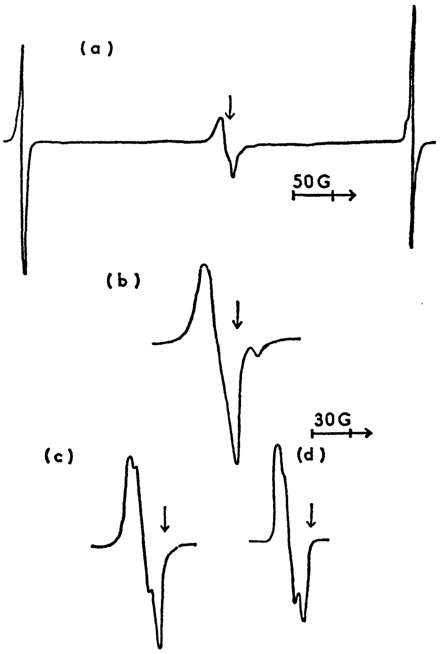


Fig. 1. ESR spectra of the radicals produced by γ irradiation of 6.5 mol dm^{-3} H_2SO_4 glassy solution of 77 K.

(a): Observed spectrum at 77 K immediately after γ irradiation.
(b): Extended spectrum of the central part of the spectrum (a).
(c): Observed spectrum at 77 K after warming above 150 K.
(d): Simulated spectrum corresponding to (c). The used parameters are given in the text. The vertical arrow indicates the position of $g=2.0036$.

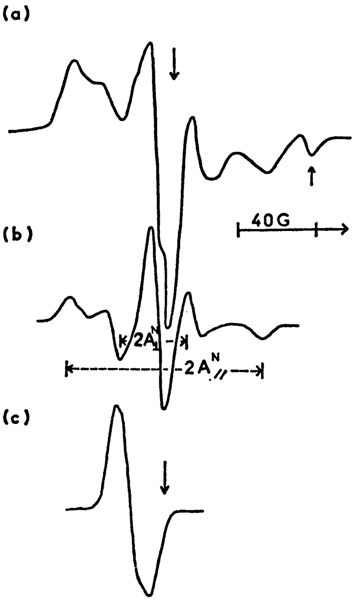
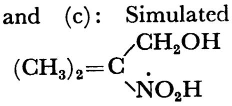


Fig. 2. ESR spectra of γ irradiated 0.5 molar solution of NMP in H_2SO_4/H_2O glasses at 77 K.
(a): Observed at 77 K.
(b) and (c): Simulated spectra of the radicals



$$(CH_3)_2{=}\dot{C}{\Big<}^{CH_2OH}_{NO_2H}$$

and $SO_4^{\cdot-}$ (or $HSO_4^{\cdot-}$) respectively.
The parameters used for this calculation are given in the text. The arrow shows (↑) a line assigned to $NO_2^{\cdot}$.

structure (Fig. 1b). Here, it is assumed for the sake of simplicity that we are only dealing with $SO_4^{\cdot-}$. A weak peak is also seen on the high field side of the central asymmetric singlet. This peak belongs most likely to the asymmetrical doublet of the residual $OH^{\cdot}$ radicals (see, for instance, Ref. 2). The signal of $OH^{\cdot}$ is completely removed upon warming of the sample above 150 K, as is shown in Fig. 1c. The spectrum of $SO_4^{\cdot-}$ has been simulated using the program of Lefebvre and Maruani[10)] and employing the optimized parameters $g_1=2.0064$, $g_2=2.0134$, $g_3=2.0192$ with a Gaussian line width $\lambda=5$ G (Fig. 1d). These principal values of the $\tilde{g}$ tensor are in good agreement with those given in Ref. 2c and the calculated second moment, $\langle \Delta H^2 \rangle_{cal}=289$ G^2, is fairly close to the experimental value, $\langle \Delta H^2 \rangle_{exp}=297$ G^2.

Radicals Formed in the Presence of Nitroalkanes: Nitromethane and NMP were irradiated in glassy sulfuric acid matrices in a concentration range from 0.01 to 0.5 mol. In both cases the yield of trapped hydrogen atoms is reduced drastically for scavenger concentrations above 0.25 mol dm^{-3}, as shown in Fig. 4d. The ESR spectrum of irradiated NMP in the H_2SO_4/H_2O glassy matrix is interpreted as the superposition of the spectra of $R\dot{N}O_2H$ and $SO_4^{\cdot-}$ radicals, as is shown in Fig. 2. Figure 2b shows that the computer simulation of the spectrum of the $R\dot{N}O_2H$ radical gives the best agreement with the experimental results when using $A_{//}^{N}=48$ G, $A_{\perp}^{N}=18$ G ($a_{iso}^{N}=28$ G) and $g_{//}=2.0035$ and $g_{\perp}=2.0075$ ($g_{iso}=2.0062$) where $A_{//}^{N}$, $A_{\perp}^{N}$, $g_{//}$ and $g_{\perp}$ are the principal values of the nitrogen hyperfine coupling tensor $\tilde{A}^{N}$ and of the $\tilde{g}$ tensor, respectively, the Gaussian line width being $\lambda=5$ G. The relevant second moment is $\langle \Delta H^2 \rangle=694$ G^2 with respect to 2.0036 (DPPH resonance). Exactly the same principal values of the $\tilde{A}_N$ and $\tilde{g}$ tensors as those previously reported for RNO_2H radicals trapped in alcohol matrices[3,4)] were obtained, confirming that a species formed by direct hydrogen atom scavenging:

$$RNO_2 + H^{\cdot} \longrightarrow R\dot{N}O_2H \qquad (1)$$

and by electron scavenging followed by protonation of the anion radical:

$$RNO_2 + e^- \longrightarrow R\dot{N}O_2^- \xrightarrow{H_3O^+} H_2O + R\dot{N}O_2H \qquad (2)$$

is involved.

Figure 2a implies that in the case of 0.5 molar NMP in H_2SO_4/H_2O glass, there is a small contribution from the direct effect of γ irradiation to the formation of the $NO_2^{\cdot}$ radical which is detected by its high-field line. The other lines together with the spectrum of the radical $(CH_3)_2{=}\dot{C}{-}CH_2OH$, which are expected to be formed simultaneously, must be hidden under the much more intense spectra of the $R\dot{N}O_2H$ and $SO_4^{\cdot-}$ radicals.

In the case of CH_3NO_2 irradiated at 77 K, the ESR spectrum of CH_3NO_2 with $A_{//}^{N}=48$ G and $A_{\perp}^{N}=18$ G is observed and the coupling $a_{\beta}^{H}=22$ G of only one proton of the methyl group is resolved (Fig. 3). The rotation of the methyl group about the C–N bond is therefore hindered and the equilibrium positions of

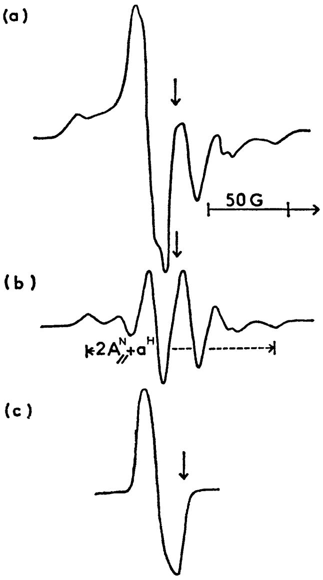
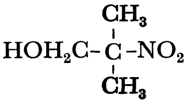


Fig. 3. ESR spectra of the radicals produced by γ irradiation of 0.5 molar solutions of CH_3NO_2 in H_2SO_4/H_2O glasses at 77 K.
(a): Spectrum observed at 77 K.
(b) and (c): Simulated spectra of radicals $CH_3\dot{N}O_2H$ and $SO_4^{\cdot-}$ (or $H\dot{S}O_4$) respectively.

TABLE 1. RADIOCHEMICAL YIELDS OF RADICALS AND MOLECULAR HYDROGEN

	G (H_2)	G ($H^{\cdot}$)	G (RNO_2H)	G ($SO_4^{\cdot-}+OH^{\cdot}$)
H_2SO_4 6.4 mol. without additive	0.7 ±0.02	1.8±0.4	—	2.2±0.5
 $HOH_2C\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}NO_2$ 0.5 mol in H_2SO_4/H_2O	0.22±0.02	≃0	2.7±1.0	2.3±0.3
CH_3NO_2 0.5 mol in H_2SO_4/H_2O	0.06±0.01	≃0	3.9±0.5	2.2±0.05

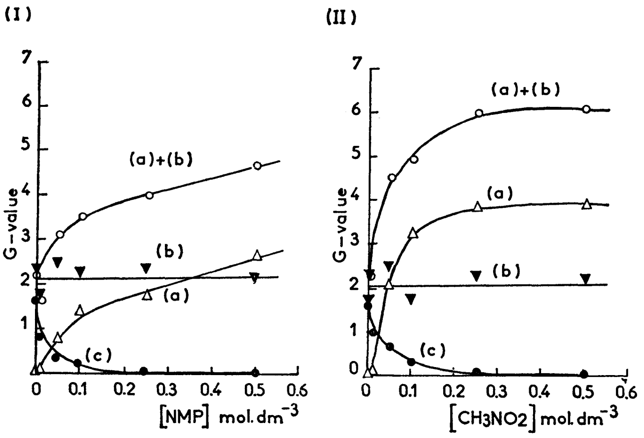
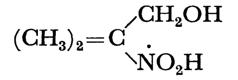


Fig. 4. G values of radicals measured at 77 K as a function of the concentration of nitroalkanes in H_2SO_4/H_2O glasses. (I) and (II) correspond to NMP and CH_3NO_2 respectively.



(a): △ $(CH_3)_2{=}\dot{C}\begin{smallmatrix}\diagup CH_2OH\\ \diagdown NO_2H\end{smallmatrix}$ or $CH_3\dot{N}O_2H$,

(b): ▼ $SO_4^{\cdot-}$ (or $HSO_4^{\cdot}$), (c): ● $H^{\cdot}$.

Irradiation dose : 2.5×10^{20} eV ml^{-1}.

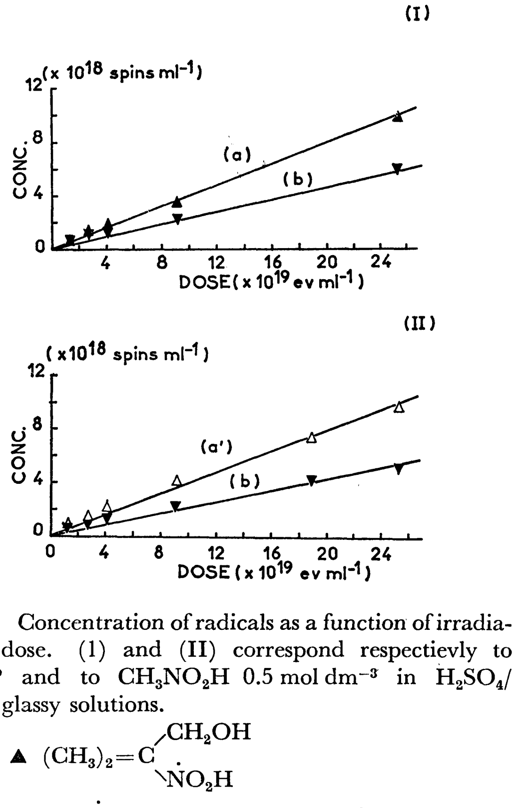
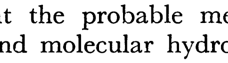


Fig. 5. Concentration of radicals as a function of irradiation dose. (1) and (II) correspond respectievly to NMP and to CH_3NO_2H 0.5 mol dm^{-3} in H_2SO_4/H_2O glassy solutions.



(a): ▲ $(CH_3)_2{=}\dot{C}\begin{smallmatrix}\diagup CH_2OH\\ \diagdown NO_2H\end{smallmatrix}$

(a'): △ CH_3NO_2H, (b): ▼ $SO_4^{\cdot-}$ ($HSO_4^{\cdot}$).

each proton correspond to the angles $\theta_1=0$ ($a_\beta^H=22.5$ G) and $\theta_2=\theta_3=\pm120°$ ($a_\beta^H=5.5$ G) where θ is the angle between the $H_\beta\diagdown$C–N plane and the axis of the nitrogen centered 2Pπ orbital of the unpaired electron. The spectrum of Fig. 3b was computed with these values of a_β^H, values of the $\tilde{A}^N$ and $\tilde{g}$ tensors which are given above and $\lambda=7$ G. The corresponding second moment is $\langle\Delta H^2\rangle=820$ G^2. The experimental spectrum of $CH_3\dot{N}O_2H$ recorded at 77 K is partially superposed on that of $SO_4^{\cdot-}$ (Fig. 3a). Upon warming, the former shows a complex structure due to the release of the intermolecular rotation about the C–N bond, as previously reported for the same radical trapped in alcohol matrices.[3]

Determination of Radiochemical Yields. Measurements of radical and molecular hydrogen yields were carried out as a function of the concentration of nitroalkanes up to 0.5 mol and of irradiation doses up to 2.5×10^{20} eV ml^{-1}, as summarized in Figs. 4, 5, 6 and in Table 1. In the absence of nitroalkanes, the radiochemical yields for trapped hydrogen atoms and molecular hydrogen were $G(H_t^{\cdot})_0=1.8\pm0.4$ and $G(H_2)_0=0.7\pm0.02$, respectively. These values are in agreement with those given by Livingston and Weinberger,[11] $G(H_t)_0=1.5$ and $G(H_2)_0=0.6$, for an identical sulfuric acid concentration of 6.4 mol dm^{-3}. on the other hand, the sum of the G values of the $SO^{\cdot-}$ and $OH^{\cdot}$ radicals was found to be 2.2±0.5 and is in satisfactory agreement with the data of Henriksen and Köhnlein.[12,13] Taking into account the probable mechanisms of formation of atomic and molecular hydrogen, as well as that of $OH^{\cdot}$ and $SO_4^{\cdot-}$ radicals,[2] it may be assumed that $G(H_t^{\cdot})\sim G(SO_4^{\cdot-}+OH^{\cdot})\simeq2$ within the limits of experimental errors.

In the case of nitroalkane glassy solutions, the central part of the ESR spectra corresponds to $SO_4^{\cdot-}$, $R\dot{N}O_2H$ and $OH^{\cdot}$. The relative yield of the RNO_2H radicals is estimated from the additivity rule of the second moments setting $\langle\Delta H^2\rangle=335$ G^2 for the composite spectrum of $SO_4^{\cdot-}+OH^{\cdot}$ (Fig. 1b) and $\langle\Delta H^2\rangle=694$ G^2 and 820 G^2 for the $R\dot{N}O_2H$ radicals from NMP and CH_3NO_2, respectively (calculated values). Figure 5 shows that the concentration of free radicals

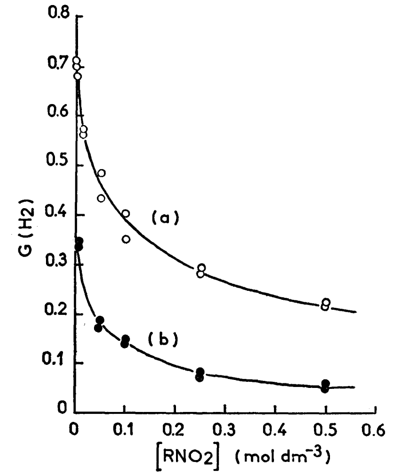


Fig. 6. G value of hydrogen molecules as a function of the concentration of nitroalkanes.
(a) and (b): Correspond respectively to the addition of NMP and CH_3NO_2. Irradiation dose : 4.2×10^{19} eV ml^{-1}.

induced by γ rays increases linearly with the irradiation dose and that no saturation tendency is observed under the present experimental conditions.

As shown in Fig. 4, the yield of $CH_3\dot{N}O_2H$ radicals increases rapidly with the nitromethane concentration up to 0.2 molar with a concomitant decay of hydrogen atoms which is no longer observed above $[CH_3NO_2]=0.25$ mol dm^{-3}. The yield of $CH_3\dot{N}O_2H$ reaches a limiting value of $G(CH_3\dot{N}O_2H)\simeq3.9$. It may be pointed out that the total limiting radical yield obtained in the presence of nitromethane is $G(R^{\cdot})\simeq6$, whereas in the absence of scavengers $G(R^{\cdot})\simeq4$. NMP is quite similar to CH_3NO_3 in following the trend that the trapped hydrogen atoms disappear completely when the concentration of the nitrocompound exceeds 0.25—0.3 mol dm^{-3}. However, NMP behaves as a less efficient electron and hydrogen atom scavenger than CH_3NO_2 since the total radical yield is $G(R^{\cdot})\simeq4$ at a maximum concentration of 0.5 mol dm^{-3}. The limiting yield of the $R\dot{N}O_2H$ radical from NMP could not be evaluated on account of the direct effect giving rise to $NO_2^{\cdot}$ at higher concentrations of NMP. An important point is that the yield of $SO_4^{\cdot-}+OH^{\cdot}$ is always of the order of 2 and independent of the concentration of added nitrocompounds (Fig. 4).

Chromatographic analysis of the molecular hydrogen yields shows that $G(H_2)$ is more efficiently reduced by CH_3NO_2 than by NMP and that it becomes negligibly small as $[CH_3NO_2]$ exceeds 0.3 mol dm^{-3}.

Discussion. It is interesting to point out that $G(H_t^{\cdot})\simeq G(SO_4^{\cdot-}+OH^{\cdot})\simeq2$ is just as in the case of alkaline glasses where $G(e_{solv.}^-)\simeq G(O^-)\simeq2.$[12] This suggests that the precursor of $H_t^{\cdot}$ is the solvated electron and that the contribution of reaction 3 is unimportant:

$$H_2O \overset{\gamma}{\rightsquigarrow} (H_2O)^* \longrightarrow H\cdot + OH\cdot \qquad (3)$$

The fact that $G(H_2)$ becomes negligibly small at nitroalkane high concentrations suggests that there is no direct formation of molecular hydrogen during γ radiolysis. On the other hand, the limiting yield of $G(CH_3\dot{N}O_2H)\simeq4$—5 obtained for nitromethane glassy solutions cannot be explained by assuming that this compound reacts directly with electrons before hydration (dry electrons). Otherwise, a concomitant increase of $G(SO_4^{\cdot-}+OH^{\cdot})$ which is produced by the precursor $(H_2O)^{\dot{+}}$ should be observed. As in the case of nitroalkanes in alkaline glass,[6] we are led to the conclusion that the yield of $CH_3\dot{N}O_2H$ radicals which exceeds 2 may be due to the scavenging of hydrogen atoms from the entity $(H^{\cdot}, H^{\cdot}, OH^{\cdot}, OH^{\cdot})$ resulting from the energetic recombination of non-hydrated primary species.[14] The $R\dot{N}O_2H$ yield is actually the same as the total yield of the hydrated and dry electrons determined in previous work on the radiolysis of water.[14]

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