BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 572—573 (1970)

ESR Spectra of Irradiated Nitroethane and Polynitroethylene

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(Received September 9, 1969)

In a previous paper[1] we have reported that the $NO_2\cdot$, $CH_2{=}\dot{C}NO_2$, nitroethylene anion radical and some other species showing a very broad ESR spectrum were observed after the γ irradiation of nitroethylene at −196°C. It has also been reported[2] that the ESR spectra of $NO_2\cdot$ and $\cdot CH_3$ were observed when nitromethane was irradiated with γ rays at −196°C and that $\cdot CH_2NO_2$ was produced after warming the sample to −143°C. Nitrogen dioxide-free radicals seem to be obtained after the radiolysis of every organic compound containing NO_2 groups, while counter radicals are not always detected by ESR spectroscopy.

In this investigation, nitroethane and polynitroethylene were irradiated with electron beams from a Van de Graaff accelerator and the ESR spectra were recorded in order to identify the free radicals produced from these compounds. The change in the ESR spectra with the increase in the temperature was also examined.

Experimental

Polynitroethylene was obtained by radiation-induced polymerization.[3] For nitroethane, we used a commercial sample from the Nakarai Chemical Co., Ltd., without further purification. The experimental techniques have already been described.[1]

Results and Discussion

Nitroethane gave the ESR spectrum shown in Fig. 1a after irradiation at −196°C. This spectrum did not change with the subsequent visible light irradiation. The asymmetric spectrum characteristic of the $NO_2\cdot$ radical can easily be distinguished. Some shoulders of the spectrum may indicate the presence of ethyl radicals.[4] The hyperfine coupling constants and g values of the $NO_2\cdot$ radical are tabulated in Table 1. These values are almost identical with those previously reported.[2,5–9] $NO_2\cdot$ radicals decayed out at about

TABLE 1. HYPERFINE COUPLING CONSTANTS AND g VALUES OF $NO_2\cdot$ RADICALS PRODUCED IN IRRADIATED NITROETHANE AND POLYNITROETHYLENE

Nitroethane	$A_x=53.9$	$g_x=2.006$
	$A_y=64.6$	$g_y=2.004$
	$A_z=43.2$	$g_z=1.992$
	$A_{iso}=53.9$	$g_{av}=2.001$
Polynitroethylene	$A_x=53.0$	$g_x=2.006$
	$A_y=64.6$	$g_y=2.004$
	$A_z=44.6$	$g_z=1.992$
	$A_{iso}=54.1$	$g_{av}=2.001$

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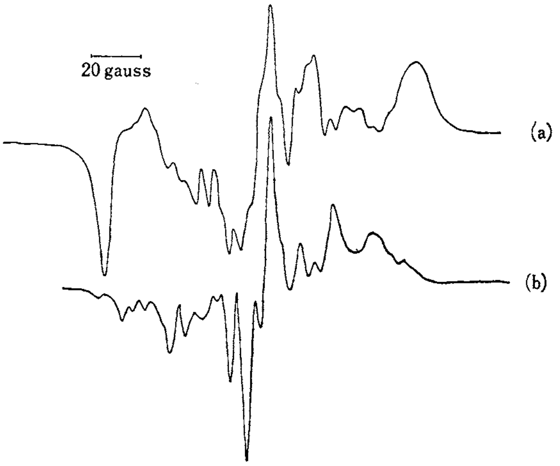

Fig. 1. ESR Spectra of irradiated nitroethane.
a) immediately after irradiation at −196°C 5×10^5 rad $G=100$
b) at −123°C $G=200$

−123°C, and there remained the spectrum shown in Fig. 1b, which may be identified as due to the $CH_3\dot{C}HNO_2$ radical. The coupling constant of the four protons is about 25 gauss, and that of nitrogen is about 7 gauss. These values should be compared with the corresponding values $a_H=20\pm1$ gauss and $a_H=6\pm1$ gauss, for the $\cdot CH_2NO_2$ radical.[2] $CH_3\dot{C}HNO_2$ radicals seem to be produced through hydrogen abstraction by ethyl radicals, since the ESR spectrum due to the $CH_3\dot{C}HNO_2$ radical, which was not observed at −196°C, appeared after the ethyl radicals had decayed out. The same mechanism has been suggested for $\cdot CH_2NO_2$ formation.[2] The spectrum due to $CH_3\dot{C}HNO_2$ radicals decayed out at about −103°C.

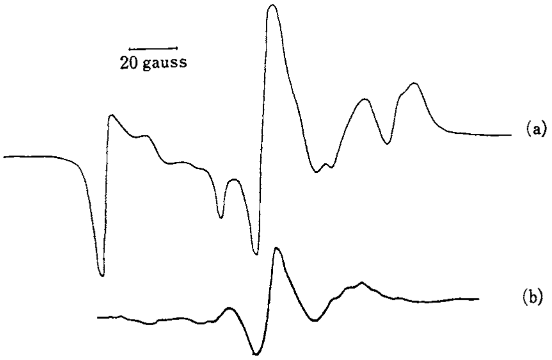

Fig. 2. ESR spectra of irradiated polynitroethylene at −196°C.
a) immediately after irradiation 5×10^5 rad $G=100$
b) after treatment at 0°C for 30 min. $G=630$

From irradiated polynitroethylene, the ESR spectrum shown in Fig. 2a was obtained at −196°C. A spectrum due to the $NO_2\cdot$ radical was clearly observed. The hyperfine coupling constants and *g* values are shown in Table 1. The $NO_2\cdot$ radical in polynitroethylene was relatively stable at −78°C, but it decayed out after treatment at 0°C for 30 min. There remained the ESR spectrum shown in Fig. 2(b), which seems to be a slightly asymmetric, five-line spectrum, and this spectrum tentatively attributed to free radicals, $-CH_2-\underset{NO_2}{\dot{C}}-CH_2-$. For this sample, however, no definite indication of the presence of the $-CH_2-\dot{C}H-CH_2-$ radicals was obtained at −196°C. Therefore, hydrogen abstraction by the $-CH_2-\dot{C}H-CH_2-$ radical at −196°C may possibly cause the formation of $-CH_2-\underset{NO_2}{\dot{C}}-CH_2-$ radicals. The observation of some shoulders which can be attributed to the later free radicals supports this mechanism.

The authors would like to express their thanks to Professor I. Sakurada for providing us with the opportunity to carry out this investigation at the Osaka Laboratories of the Japanese Association for Radiation Research on Polymers, which is now known as the Osaka Laboratories for Radiation Chemistry, Japan Atomic Energy Research Institute, and to Mr. H. Yamaoka for his kindness in giving us polynitroethylene.