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Summary

N-oxidation of 5-amino-3,4-dichloropyridazine and 4-amino-3,5-dichloropyridazine gave their 1-oxides. The amino groups on 3-, 4-, 5-, and 6-positions of pyridazine 1-oxide were substituted with chlorine or bromine by diazotization, but yield of 3-bromopyridazine 1-oxide was poor. 5-Amino-3,4-dichloropyridazine 1-oxide is usable as the starting material for the preparation of 5-substituted pyridazine 1-oxides.

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Masaichiro Masui and Hiroteru Sayo: Electron Spin Resonance of Free Radicals Electrochemically Generated from Polynitroalkanes.[*1]

(*Faculty of Pharmaceutical Sciences, Osaka University*[*2])

In the past several years, fairly many studies have been reported on the electron spin resonance (ESR) spectrum of aromatic nitro anion radicals,1) but a few were reported on aliphatic nitro anion radicals,2~6) especially on the radicals derived from aliphatic polynitro compounds only two papers being found. According to Adams, *et al.*2) 2,2-dinitropropane gave no signal but tetranitromethane and dinitromethane gave well resolved spectra which were thought to be composed of several structures, but they did not give their hyperfine structures and isotropic coupling constants either. More recently, Lagercrantz6) observed that a free radical produced by the reduction of tetranitromethane with sodium dithionite in alkaline aqueous solution showed an ESR spectrum of seven equally spaced lines (intensity ratio 1:3:6:7:6:3:1), from which they found the nitrogen coupling constant was 8.4 gauss and deduced that the radical was $[(NO_2)_3C\cdot]^{2-}$.

[*1] This paper is the Part Ⅻ of "Controlled Potential Electrolysis" (Part Ⅺ, M. Masui, H. Sayo, K. Kishi: Tetrahedron, **21**, 2831 (1965).

[*2] Toneyama, Toyonaka-shi, Osaka-fu (桝井雅一郎, 佐用博照).

1) *a*) D.H. Geske, A.H. Maki: J. Am. Chem. Soc., **82**, 2671 (1960). *b*) A.H. Maki, D.H. Geske: J. Chem. Phys., **33**, 825 (1960). *c*) *Idem*: J. Am. Chem. Soc., **83**, 1852 (1961). *d*) I. Bernal, G.K. Fraenkel: *Ibid.*, **86**, 1671 (1964), and many others.

2) L.H. Piette, P. Ludwig, R.N. Adams: J. Am. Chem. Soc., **84**, 4212 (1962).

3) *Idem*: Anal. Chem., **34**, 917 (1962).

4) A.K. Hoffman, W.G. Hodgson, W.H. Jura: J. Am. Chem. Soc., **83**, 4675 (1961).

5) A.K. Hoffman, W.G. Hodgson, D.L. Maricle, W.H. Jura: *Ibid.*, **86**, 631 (1964).

6) C. Lagercrantz: Acta Chem. Scand., **18**, 382 (1964).

In the previous studies,[7~9] we revealed the electrochemical reduction processes of several polynitroparaffins, and, during the studies, we believed possibility of existence of fairly stable free radicals as the intermediate. In the present paper we have studied the ESR spectra of radicals produced by electrolytic reduction of 1,1,1-trinitroethane (TNE) and 1,1-dinitroethane (DNE), and analyzed their hyperfine structures.

Results and Discussion

Because of the instability of the produced radicals in aqueous buffer solution used in the previous electrochemical studies, no attempt was succeeded except for the runs carried out in 50% aqueous acetonitrile. TNE shows well resolved spectra of 36 lines by the electrolysis at -1.5 v. *vs.* SCE and its hyperfine pattern exhibits three fold symmetry, which suggests the existence of one dominant nitrogen coupling constant (Radical I: see Fig. 1a). A very good fit of the observed spectrum is obtained by assuming $a_N=13.99$, $a_{N'}=3.50$, $a_{H(d)}=3.50$, $a_{H(t)}=1.11$ gauss where a_N and $a_{N'}$, $a_{H(d)}$, and $a_{H(t)}$ are each an interaction with ^{14}N nucleus, a single proton, and two equivalent protons, respectively (Fig. 1b). Electrolysis at less negative potentials than above gave no spectrum.

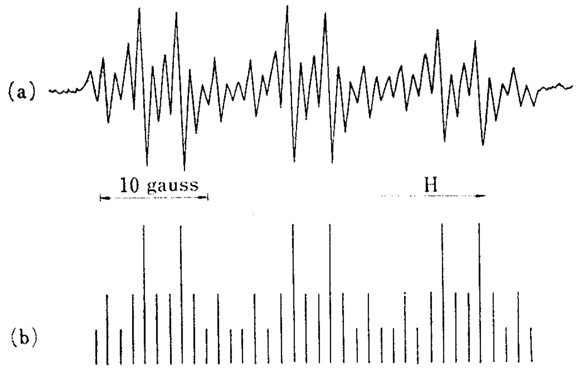

Fig. 1. (a) Derivative of the Electron Spin Resonance Spectrum of the Radical I Obtained from 1,1,1-Trinitroethane by Electrolytic Reduction
(b) Spectrum Calculated Using Coupling Constants Shown in the Text

The heights of the component lines are proportional to the calculated relative intensities.

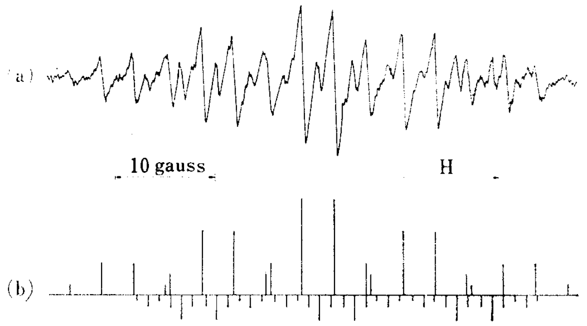

Fig. 2. (a) Derivative of the Electron Spin Resonance Spectrum of the Radicals Obtained from 1,1-Dinitroethane by Electrolytic Reduction
(b) Constructed Absorption Spectra

One above the base line is calculated from $a_N=10.11$ (quintet) and $a_H=3.18$ gauss (quartet); that below the base line is from $a_N=13.87$, $a_{N'}=3.49$, $a_{H(d)}=3.49$ (doublet) and $a_{H(t)}=1.10$ gauss (triplet).

1,1-Dinitroethane potassium salt (DNE·K salt) shows complicated spectrum when the cathode potential is increased above -1.0 v. *vs.* SCE, but its hyperfine pattern does not exhibit three fold symmetry, and thus it is suggested that two or more different radicals are contributing (Fig. 2a). Because the first step of the electrolytic reduction processes of TNE in aqueous buffer solution is a two-electron reduction producing the aci-nitro ion of DNE and the second step is a further reduction of this aci-nitro ion, the same radical must be produced in either electrolytic reduction. Subtraction of the 36 lines corresponding to the spectrum obtained with TNE ($a_N=13.87$, $a_{N'}=3.49$, $a_{H(d)}=3.49$, $a_{H(t)}=1.10$) from that obtained with DNE·K salt leaves a spectrum composed of 20 lines with $a_N=10.11$ (interaction with two equivalent ^{14}N nuclei), and $a_H=3.18$ (interac-

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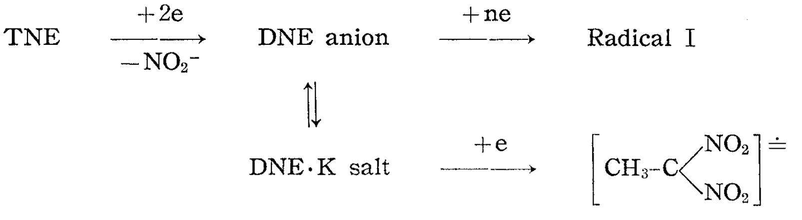
7) M. Masui, H. Sayo: J. Chem. Soc., **1961**, 4773.
8) *Idem*: *Ibid.*, **1961**, 5325.
9) *Idem*: *Ibid.*, **1962**, 1733.

tion with three equivalent protons). This spectrum is assumed to be derived from dianion radical $\left[\mathrm{CH_3{-}C}\genfrac{}{}{0pt}{}{\mathrm{NO_2}}{\mathrm{NO_2}}\right]^{\dot{=}}$ which is produced by one-electron reduction of aci-nitro ion of DNE. The a_N of this radical is less than one half of that of mononitroparaffin anion radicals, but this seems reasonable, because in aromatic nitro compounds a_N values observed for radicals derived from dinitro compounds are generally in the range of one half to one sixth of those observed with mononitro anion radicals.[1b,1c] Because the α carbon atom is sp^2 hybridized, the pseudo π orbital of the methyl group can conjugate with the $2p\pi$ orbitals of the nitrogen atoms. The larger proton coupling constant of the methyl group attached to α carbon atom compared with that of mononitroparaffin anion radicals can be explained on the basis of the hyperconjugation effect of the methyl group.

The structure of radical I observed in the reduction of TNE and also in that of DNE·K salt is not clear at the present stage; and further studies are needed to decide whether this radical is a one-electron reduction product or a further reduced product of DNE.

The fact that no DNE dianion radical was observed in the reduction of TNE may be explained by assuming that DNE produced by the first reduction step of TNE is one of two forms of DNE and this is much more easily reducible than DNE·K salt (Scheme 1).



(1)

Experimental

Electron spin resonance measurements were performed at X-band frequencies using a spectrometer Model JES-3B-365, manufactured by the Japan Electron Optics Co. employing 100 kc. field modulation. The cell for electrogeneration was similar to that used by Adams, *et al.*[3] Generations were performed in the microwave cavity of the ESR spectrometer using the technique of Geske and Maki.[1a] Hyperfine coupling constants were measured by careful comparison with the splitting of Mn^{2+} in magnesium oxide. The value of 86.8 gauss was taken for the Mn^{2+} splitting. Preparation and purification of polynitroparaffins were previously given.[8,9]

Samples were dissolved in 50% aqueous acetonitrile solution containing $0.1M$ potassium chloride as the supporting electrolyte to $5\ mM$. Cathode potentials were controlled against a saturated calomel electrode. Oxygen in the cell and dissolved in the solution was removed by purified nitrogen gas.

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