

CONTROLLED POTENTIAL ELECTROLYSIS—XIV*

ELECTRON SPIN RESONANCE SPECTRA OF FREE RADICALS GENERATED ELECTROCHEMICALLY FROM SEVERAL ALIPHATIC TERTIARY NITRO COMPOUNDS

H. SAYO and M. MASUI

Faculty of Pharmaceutical Sciences, Osaka University, Toyonaka, Osaka-fu, Japan

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Abstract—Six aliphatic tertiary nitro compounds were reduced electrolytically in acetonitrile, and their electron spin resonance spectra studied. *t*-Nitrobutane, 2-methyl-2-nitro-1-propanol and tris(hydroxymethyl)nitromethane gave the ESR spectra of tertiary nitro anion radicals, showing only one ^{14}N splitting during electrolysis, but α -nitroisobutyramide gave a 6-line spectrum showing one ^{14}N and one proton splitting. The 6-line spectrum was assigned to the 2-nitropropane anion radical which was produced by decomposition of the anion radical of α -nitroisobutyramide. Di-alkylnitroxides were obtained from all the above compounds after electrolysis, but tris(hydroxymethyl)nitromethane and α -nitroisobutyramide gave in addition another unidentified radical. Ethyl α -nitroisobutyrate and α -nitroisobutyronitrile gave no ESR spectrum either during or after electrolysis.

PART XIII¹ described the electrochemical reduction of aliphatic *t*-nitro compounds in acetonitrile by polarography and large scale controlled potential electrolysis, and it was suggested that the first step of the electrode process involved a one-electron transfer leading to an unstable nitro anion radical, which cleaved to the nitrite ion and the corresponding free radical.¹ The present paper reports results obtained by controlled potential electrolysis carried out in a resonance cavity of an ESR spectrometer, and the stability and decomposition of *t*-nitro radicals is discussed.

RESULTS

t-Nitrobutane (I). The result obtained was the same as that reported by Hoffmann *et al.*^{2,3}

2-Methyl-2-nitro-1-propanol (II). Electrolysis of a 0.01M solution of this compound at -1.8 V resulted in a strong 3-line spectrum ($A^{\text{N}} = 26.5$ gauss) at the outset of electrolysis (Fig. 1(a)). On discontinuing the electrolysis, the spectrum of the nitro anion radical disappeared rapidly with the appearance of another 3-line spectrum ($A^{\text{N}} = 15.2$ gauss), and the intensity of this spectrum grew stronger with time and reached its maximum value in 30 minutes (Fig. 1(b)). This spectrum did not change further.

Tris(hydroxymethyl)nitromethane (III). Electrolysis of this compound at -1.5 V resulted in a weak 3-line spectrum ($A^{\text{N}} = 26.0$ gauss) at the outset of electrolysis (Fig. 1(c)). After stopping the electrolysis, the spectrum was rapidly replaced by an 11-line spectrum (Fig. 1(d)), which was interpreted as arising from a mixture of two

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radicals, because the intensity ratio of the components changed with the conditions of electrolysis. The spectrum was assigned to a 3-line spectrum ($A^N = 13.2$ gauss) and a 9-line one ($A^N = 14.8$ gauss and A^H (two proton) = 16.6 gauss) the center lines of which were superimposed.

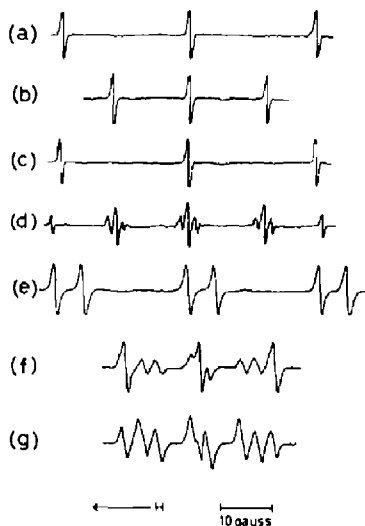


FIG. 1. ESR spectrum from the electrolytic reduction of:

- (a) 2-methyl-2-nitro-1-propanol, during the electrolysis;
- (b) 2-methyl-2-nitro-1-propanol, after stopping the electrolysis;
- (c) tris(hydroxymethyl)nitromethane, during the electrolysis;
- (d) tris(hydroxymethyl)nitromethane, after stopping the electrolysis;
- (e) α -nitroisobutyramide, during the electrolysis;
- (f) α -nitroisobutyramide, after stopping the electrolysis;
- (g) α -nitroisobutyramide, after stopping the electrolysis at a different position of mercury pool cathode.

α -Nitroisobutyramide (IV). Electrolysis of a 0.02M solution of this compound at -1.7 V for about 10 minutes resulted in a weak 6-line spectrum ($A^N = 25.7$ gauss and $A^H = 5.1$ gauss) (Fig. 1(e)). After stopping the electrolysis, this spectrum disappeared rapidly and no other spectrum appeared for several hours. After about 6 hours, the solution developed a 9-line spectrum which reached its maximum intensity in about 12 hours (Fig. 1(f)). This 9-line spectrum was interpreted as being due to a mixture of two radicals which showed a 3-line spectrum ($A^N = 14.6$ gauss) and a 6-line one ($A^N = 9.6$ gauss and $A^H = 2.9$ gauss), because the intensity ratio of the components varied with the position of the mercury pool cathode in the resonance cavity (Fig. 1(g)).

Ethyl α -nitroisobutyrate (V) and α -nitroisobutyronitrile (VI). These compounds showed no ESR spectrum during electrolysis at -1.5 , 2.0 V or for a long period after stopping the electrolysis.

2-Nitropropane (VII). Electrolysis of a 0.02M solution at -1.8 V gave a weak

6-line spectrum ($A^N = 25.7$ gauss and $A^H = 5.1$ gauss). On discontinuing the electrolysis, the spectrum disappeared rapidly and no other spectrum was observed even after the solution was kept for a long time.

DISCUSSION

The ESR spectra observed during the electrolysis of nitro compounds at the plateau potential of their polarographic first wave is generally considered to arise from a nitro anion radical which is produced by a one-electron reduction of the parent compound. I, II and III gave similar 3-line spectra with a ^{14}N hyperfine coupling constant (h.c.c.) which seemed reasonable for aliphatic nitro anion radicals, but IV gave a 6-line spectrum with one proton splitting. Since IV has no proton on the α -C atom, the additional proton splitting should be attributed to a proton from the amide group which is hydrogen-bonded with an O atom of the nitro group, as shown in Fig. 2. The unpaired electron spin density on this O atom was calculated to be 0.103

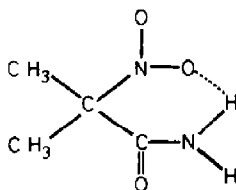
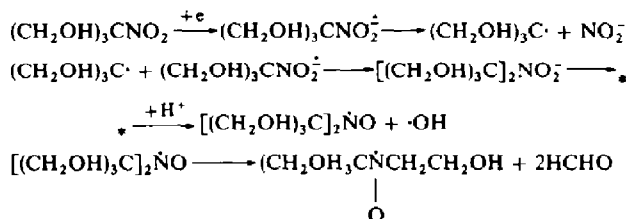


FIG. 2.

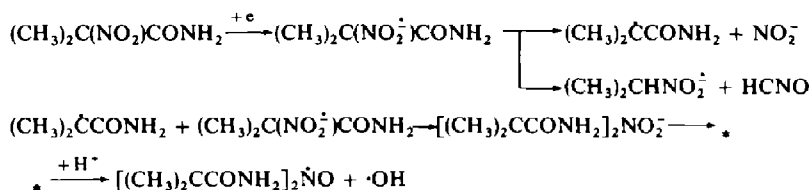
by the extended Hückel MO calculation,¹ and hence the h.c.c. of the proton of the amide group was calculated to be 0.8 gauss if 8 gauss⁴ was used as the spin polarization parameter of the O—H bond, Q_{OH}^H . An example of a proton h.c.c. of this type is the nitrobenzene free radical which is reported to be 0.38 gauss.⁵ The experimental value of 5.1 gauss is much larger than those reported. Moreover, the anion radicals of II and III showed no proton splitting whereas they may also have similar hydrogen-bonding. The observed proton splitting, therefore, was concluded not to be derived from this type of proton. On the other hand, the bond between the α carbon and carbonyl carbon of IV has been found to cleave readily in alkaline solution.⁶ Thus a part of the anion radical of IV is also assumed to be decomposed to the 2-nitropropane anion radical and isocyanic acid. As the ESR spectrum obtained on electrolysis of IV both in acetonitrile and N,N-dimethylformamide agreed well with that from VII, the former is concluded to be that of the 2-nitropropane anion radical. The radical observed after stopping the electrolysis of II is believed to be a nitroxide radical from its stability and ^{14}N h.c.c.; the nitroxide must have been produced through similar steps to those suggested for the formation of di-*t*-butylnitroxide by Hoffmann *et al.*^{2, 3} In the case of III, however, two radicals were found. One of them had been split with only one ^{14}N and is suggested to be di[tris(hydroxymethyl)methyl]nitroxide. The other had been split with one ^{14}N and two equivalent protons, and is assumed to be tris(hydroxymethyl)methyl- β -hydroxyethylnitroxide (Scheme 1).

SCHEME 1



There are some doubts about the proton h.c.c. of the latter radical, because it is much larger than that of di-*n*-hexylnitroxide.⁷ Electrolysis of IV also gave two radicals after stopping the electrolysis. One had been split with only one ¹⁴N and is suggested to be di(1-methyl-1-carbamoyl-ethyl)nitroxide. Since electrolysis of 2-nitropropane gave no ESR spectrum after stopping the electrolysis, the anion radical of IV must be sufficiently stable to produce the nitroxide through Scheme 2 even though its existence was not detected by ESR.

SCHEME 2



The other had been split with one ¹⁴N and one proton, and furthermore its ¹⁴N h.c.c. is much smaller than that of ordinary aliphatic nitroxides. The structure of this radical is not clear at present. The fact that V and VI gave no ESR spectrum either during or after electrolysis is surely due to the instability of their nitro anion radicals. However the reason why the anion radicals of V and VI are more unstable than that of IV is not clear.

EXPERIMENTAL

Materials. *t*-Nitro compounds were prepared and purified as described.^{1,8} Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (TEAB) and perchloric acid, and recrystallized from water.⁹ Acetonitrile was purified by the method of O'Donnell *et al.*¹⁰ The acetonitrile soln containing 0.1M TEAP or TEAB was dried further by the method of Arther and Haynes.¹¹ The dried soln contained 0.0003% water as determined by Karl Fischer titration.

Apparatus. ESR spectra were obtained with a JEOL P-10 spectrometer employing a 100 kc field modulation. Hyperfine coupling constants were measured by careful comparison with the splittings of a fresh soln of peroxyamine disulfonate. The value of 13.00 gauss was taken as the value for nitrogen splitting. Recorded coupling constants are usually the average values of 2 or 3 spectra. The precision of the coupling constant is believed to be ± 0.1 gauss.

Generation of free radicals. The electrolytic cell used for radical generation was similar to that used by Geske and Maki.¹² Acetonitrile was used as solvent except when otherwise indicated. TEAP or, in some instances, TEAB was used as the supporting electrolyte. The electrolysis was carried out at a constant potential, which was selected on the basis of polarographic measurements. The applied potentials were

measured with respect to an aqueous saturated calomel electrode. All solns were thoroughly deaerated before electrolysis by passage of purified argon for at least 1 hr. The argon (Ar 99.99%, N₂ 0.005%) was passed through Cu turnings (heated to 400°), then acetonitrile soln and finally the test soln.

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