BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 277—278 (1971)

Anion Radicals Produced by the Non-aqueous Polarographic Reduction of Several Benzonitrile *N*-Oxides[1]

Hiroshi Miyazaki, Koichi Nishikida, and Tanekazu Kubota
Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka

(Received July 14, 1970)

Anion and cation free radicals and their structures, produced by the controlled potential electrolysis of heterocyclic amine *N*-oxides, have been extensively studied in our laboratory.[2] It has usually been found that the anion[2a-d] or cation[2e] free radical of the mother compound is produced at the first reduction or oxidation wave respectively. We have now extended this kind of study to several benzonitrile *N*-oxides whose electronic structures and physicochemical properties[3] have also been investigated in detail in comparison with such other amine oxides as pyridine *N*-oxide and nitrone. The experimental results obtained here, however, are somewhat different from those previously reported.[2] In this note we will report on the non-aqueous polarographic behaviour of the substituted benzonitrile *N*-oxides listed in Table 1, and on the electron-spin-resonance (ESR) spectra and their analyses of anion radicals produced by the controlled potential electrolysis of the nitrile *N*-oxides.

Of the samples, the 4-nitro-2,6-dimethyl-benzonitrile *N*-oxide (**5**) was prepared by the well-known Grundmann method[4] from 4-nitro-2,6-dimethylbenzoaldoxime and NaOBr, the corresponding nitrile (**10**) (see Table 1) being obtained by the deoxygenation of the above nitrile *N*-oxide with $(CH_3O)_3P$.[4] The other samples used and the experimental techniques were the same as those described in our previous papers.[2,5] As a typical example, in Fig. 1 we show the polarograms of 2,4,6-trimethylbenzonitrile *N*-oxide (**2**) and the corresponding nitrile (**7**) and the ESR spectrum obtained by electrolysis at the second wave of **2**. All the other experimental data are included in Table 1. We can see from Fig. 1 that the wave height of the first reduction wave of the DC polarogram of **2** is substantially larger than that of the second wave. For the case of the AC polaro-

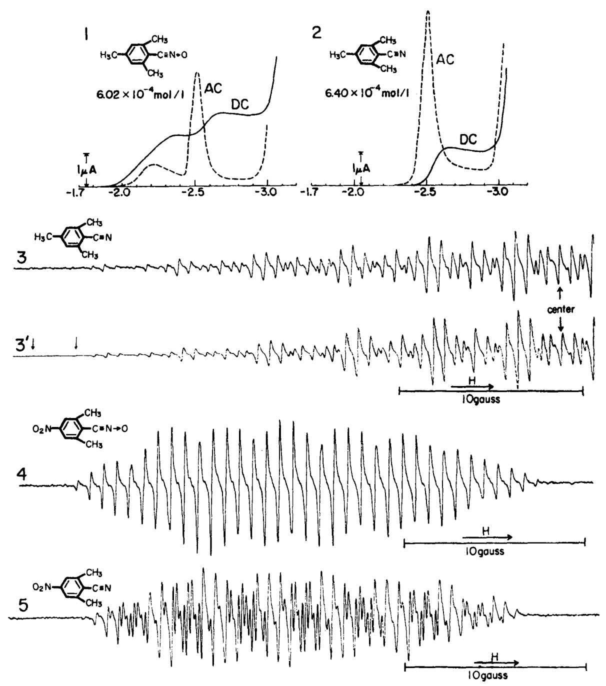

Fig. 1. ESR spectra of the anion radicals and non-aqueous polarograms of the compounds given in this figure. Simulated half spectrum for the observed one (3) is shown in the spectral number 3′ where vertical arrows indicate that the weak signals (1 : 2 : 1 triplet) also appear at these positions (hfc constant values used are listed in Table 1).

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[1] Presented in part at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

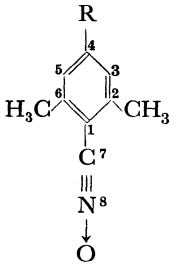
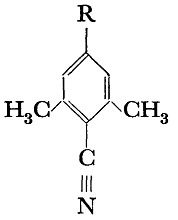
[2] a) T. Kubota, H. Miyazaki, and Y. Mori, *Rev. Polarog.* (Kyoto), **14**, 313 (1967). b) T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Ōishi, *J. Amer. Chem. Soc.*, **90**, 5080 (1968). c) T. Kubota, Y. Ōishi, K. Nishikida, and H. Miyazaki, This Bulletin, **43**, 1622 (1970). d) K. Ezumi, H. Miyazaki, and T. Kubota, *J. Phys. Chem.*, **74**, 2397 (1970). e) K. Nishikida, T. Kubota, H. Miyazaki, and S. Sakata, Presented at the 8th Symposium of Electron Spin Resonance held by the Chemical Society of Japan, Hiroshima, Nov., 1969, to be published.

[3] See M. Yamakawa, T. Kubota, and H. Akazawa, *Theor. Chim. Acta*, **15**, 244 (1969) as a leading reference.

[4] C. Grundmann and J. M. Dean, *Angew. Chem. Int. Ed. Engl.*, **3**, 585 (1964); *J. Org. Chem.*, **30**, 2809 (1965); C. Grundmann and H. D. Frommeld, *ibid.*, **30**, 2077 (1965). The authors wish to express their thanks to Mrs. H. Ishida (née Akazawa) for preparing these samples.

[5] M. Yamakawa, T. Kubota, and H. Akazawa, This Bulletin, **40**, 1600 (1967).

Table 1. Non-aqueous polarographic data, observed hyperfine coupling constants of produced anion radicals, and their assignments of the compounds shown in this Table

Compound	R	No.	Mp °C	$-E_{1/2}$: V *vs.* SCE (Lingane's constant)[a) 1st wave	$-E_{1/2}$: V *vs.* SCE (Lingane's constant)[a) 2nd wave	AC peak-height[a) μmhos/mmol 1st wave	AC peak-height[a) μmhos/mmol 2nd wave	Hyperfine coupling constants (absolute value) of the corresponding anion radicals[a)
	H	1	79.5—81.0	1.95[b) (1.68)	2.38 (1.31)	12	134	[c)
	CH_3	2	110.0	2.12[b) (2.64)	2.52 (1.32)	20	125	[c)
	Br	3	100.0—101.5	1.90[b) (2.43)	2.39 (0.99)	27	49	[c)
	OCH_3	4	69.0—71.0	2.24[b) (2.01)	2.62 (1.73)	14	69	—
	NO_2	5	130.0—131.0	0.915 (1.04)	1.132 (0.44)	213	85	6.02(4-NO_2), 3.71(3,5), 1.52(8), 0.74(2,6-CH_3)
	H	6	88.5—89.0	2.403 (2.22)	—	195	—	8.49(4), 3.87(2,6-CH_3), 2.41(8), 0.40(3,5)
	CH_3	7	50.0—51.5	2.505 (2.15)	—	189	—	9.52(4-CH_3), 4.10(2,6-CH_3), 2.38(8), 0.66(3,5)
	Br	8	69.0—70.0	1.849 (3.97)	2.367 (2.29)	52	223	[c)
	OCH_3	9	70.0—71.5	2.592 (3.39)	—	92	—	—
	NO_2	10	120—122	0.879 (2.14)	1.706 (1.86)	406	289	6.46(4-NO_2), 2.96(3,5), 0.82(8), 0.63(2,6-CH_3)

a) All measurements were made in dimethylformamide containing tetra-*n*-propylammonium perchlorate 0.1 mol/*l*. Here, Lingane's constant, *I*, was calculated by the equation $I(=607n\sqrt{D})=i_d/(cm^{2/3}t^{1/6})$, were i_d and c are wave height (μA) of diffusion current and sample concentration (mM), respectively. *m* (mg/sec) and *t* (sec/1 drop) are well-known characteristics of dropping mercury electrode. The *t* value was measured at the potential of diffusion current, but the *m* value in open circuit was approximately adopted.

b) The shape of the first wave is quite far from that of a normal one electron reduction wave as is seen in Fig. 1-1. Especially, for R=H the first wave seems to be divided into two waves. The former value is in this Table and the latter would be $E_{1/2}\approx-2.13$ V (0.90) and AC peak-height ≈ 6.

c) See discussions in the text.

gram, however, the above relationship between the first and second waves is just the reverse, the second peak height being considerably higher. In addition, the half-wave reduction potential values, $E_{1/2}$, of **2** and **7** are in almost the same order if a comparison is made between the second wave of **2** and the first wave of **7**. When controlled potential electrolysis has been made at the second reduction wave of **2**, one can obtain the well-resolved ESR spectrum shown in Fig. 1, which has the same pattern as that obtained by the electrolysis at the first wave of **7**. Therefore, we see that the anion radical of 2,4,6-trimethylbenzonitrile is produced there. On the other hand, no ESR signal was observed when the electrolysis was made at the first wave of **2**. Behaviour similar to the above was also found in the compound **1** (see Table 1).

All of the experimental facts mentioned above suggest the conclusion that the first wave of nitrile *N*-oxides is due to the deoxygenation process of the $-C\equiv N\rightarrow O$ group, which is behaviour similar to that observed in an aqueous medium,[2a) and that the second wave may be due to the anion-radical formation of the deoxygenated nitrile compound. This fact is quite different from the case of heterocyclic amine *N*-oxides, where the first reduction wave is due to the anion-radical formation of mother compounds, as is often the case. In the case of compound **3**, it was observed that the deoxygenation and debromination occur at the same time at the first reduction wave. The assignment of the hyperfine coupling (hfc) constants given in Table 1 is straightforward from the point of view of the molecular symmetry and the number of atoms which are in the same chemical environment, and seems to be reasonable in terms of theory.

The only exceptional compound in the present experiments is 2,6-dimethyl-4-nitrobenzonitrile *N*-oxide (**5**), whose anion radical was observed at the first reduction wave. The ESR spectrum obtained is well resolved, but is quite different from that of the anion radical of the corresponding nitrile (**10**). These spectra are shown in Fig. 1.[6) The fact that the oxygen atom of the nitrile-oxide group is very reactive[5,7) may be responsible for the deoxygenation process at the first wave. For the molecule **5**, however, the large intramolecular charge-transfer effect[3,5) from the nitrile-oxide group oxygen atom to the nitro group may stabilize the $\equiv N\rightarrow O$ bond more effectively; thus, the anion radical of the mother compound **5** is produced.

The authors wish to express their thanks to Professors Soichiro Musha and Makoto Munemori of the College of Engineering, University of Osaka Prefecture, for their useful discussions.

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6) Detailed discussions of all the hfc constant values in this case (see Table 1) will be made in a separate paper, where they will be compared with the anion radical data of nitrones having a nitro group, *etc.*

7) R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, **2**, 565 (1963).