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CYCLIC VOLTAMMETRY AND ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF P-IODONITROBENZENE ANION RADICAL IN METHYLISOBUTYLKETONE

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Electron paramagnetic resonance (EPR) spectra of p-iodonitrobenzene anion radical was obtained in methylisobutylketone(MIBK) using tetrabutylammonium perchlorate(TBAP) as a supporting electrolyte. The line broadening of EPR spectra of p-iodonitrobenzene anion radical is considered to be caused by the ion pair formation between supporting electrolyte cation and radical anion.

The formation of nitrobenzene anion radical and halide ion upon electrochemical reduction of halonitrobenzene in dimethylformamide(DMF) was reported by Adams et al.$^{1)}$ and others$^{2)}$. Author also investigated the voltammetry and EPR spectra of p-iodonitrobenzene in DMF-water mixture$^{3)}$. MIBK has been investigated as a solvent for a polarographic use$^{4)}$. This paper concerns the voltammetry and EPR study of p-iodonitrobenzene in MIBK.

Experimental A Yanagimoto P-8 Polarograph was used with a hanging mercury drop electrode. Potential sweep rate was 2 volt or 4 volt per 1.1 minutes at 25°C. A Varian 4502-15 type or A Nihon Denshi Jes-ME-3X type EPR apparatus was used. The electrolysis at - 1.5 volt(vs.SCE) was carried out by internal generation technique. A spiral platinum anode was used. A reference electrode was an aqueous saturated calomel electrode. Eastmann TBAP was recrystallized from ethanol three times and then dried under the reduced pressure. All measurements were done in the dry box$^{5)}$. Highly purified nitrogen was used during all measurements.

Results and Discussion Cyclic voltammogram of p-iodonitrobenzene in MIBK containing 0.1 M TBAP shows an almost reversible redox couple at the first peak. The second wave shows only a very small peak or almost disappears. Therefore,the rate constant for the abstraction of a hydrogen atom is considered to be much slower than that in DMF,AN or DMSO$^{6)}$ and p-iodonitrobenzene anion radical could fairly be stabilized in MIBK even at room temperatures, although thermodynamically unstable p-iodonitrobenzene anion radical could in fact be stabilized only at low temperatures7). Coupling constant of p-iodonitrobenzene anion radical and nitrobenzene anion radical produced successively by the controlled potential electrolysis at - 1.5 volt vs. SCE are shown in Table 1. Nitrogen coupling constant in MIBK is much larger than that in DMF.

Table 1. Coupling constants of anion radicals in DMF and MIBK

solvent	substance	coupling constant (gauss)			
		a_N	$a_{H,o}$	$a_{H,m}$	$a_{H,p}$
MIBK	p-iodonitrobenzene	14.14	3.14	0.82	-----
MIBK	nitrobenzene	10.45	3.36	1.02	4.10
DMF	nitrobenzene	9.79	3.36	1.09	3.94

supporting electrolyte : 0.1 M TBAP

From the consideration of the incomplete dissociation of TBAP in MIBK4),another physical deformation except twisting effect3) which may be caused by ion pair formation between nitro group anion radical and supporting electrolyte cation should be considered in case of p-iodonitrobenzene8)9). The nitro group must be dislocated to accomodate the added bulky group and is reflected in the increase of a_N and the decrease in ring proton couplings when ion pair is formed. No cation couplings are observed in the EPR spectra owing to a rapidly exchanging cation system10). EPR spectra in MIBK also shows a line broadening effect most markedly observed in the odd spin states of the nitrogen,although a remarkable line broadening is observed only in the case of lithium ion or magnesium ion as a supporting electrolyte cation in DMF8).

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