

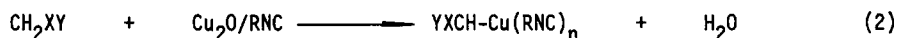
ELECTRON TRANSFER FROM COPPER-ISONITRILE COMPLEX PRODUCING RADICAL ANION

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(Received in Japan 5 February 1974; received in UK for publication 25 February 1974)

In the course of our studies¹ on the synthetic reactions caused by copper-isonitrile complexes, it has been found that metallic copper and Cu₂O react in the presence of isonitrile with the so-called active methylene compounds to produce the corresponding organocopper isonitrile complexes together with H₂ gas or H₂O, respectively, according to eqs 1 and 2.



X, Y = CO₂R', COR', CN etc.

Most organocopper isonitrile complexes thus prepared are not sufficiently stable to be isolated. However, in the reaction of cyclopentadiene with Cu₂O in the presence of isonitrile, a stable pentahapto-cyclopentadienylcopper(I) isonitrile has been isolated.^{1a} Organocopper isonitrile complexes react with α,β -unsaturated carbonyl and nitrile compounds in the manner of the Michael reaction² and with ketones and aldehydes in the manner of aldol condensation.^{1a}

The generation and reactivities of organocopper isonitrile complexes mentioned above resemble superficially those of organometallics of alkali metals. This observation prompted us to examine esr spectra of the systems of copper-isonitrile complex and Cu₂O-isonitrile complex with various π -substrate. Herein, we wish to report an electron transfer from metallic copper and Cu₂O to π -substrates producing the corresponding radical anions under mild conditions in the presence of isonitrile. Esr spectra of a mixture of metallic copper or Cu₂O and π -substrates such as p- and m-dinitrobenzene, nitrobenzene, benzoquinone,

fluorenone and tetracyanoethylene (TCNE) in isonitrile exhibited the resolved signals of the corresponding organic radical anion. Easy occurrence of the electron transfer may be due to the substantial reduction of ionization potential of metallic copper and Cu_2O due to the isonitrile ligand. To our best knowledge, the formation of organic radical anions in the reaction of metallic copper or Cu_2O with π -substrates has been unprecedented except for a combination of metallic copper and TCNE or tetracyanoquinodimethane,³ which are very strong π -acids.

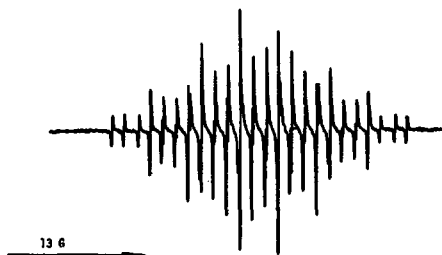
A typical procedure of the preparation of an esr sample is as follows. A glass tube containing 1 mg atom of metallic copper or 1 mmol of Cu_2O , 3 mmol of tert-butyl isocyanide and 0.1 mmol of p-dinitrobenzene was sealed off after three freeze-thaw cycles on a vacuum line. ESR spectrum was taken with a JEOL-JES-3BSX. The representative well-resolved ESR spectrum is shown in Figure 1.

The hyperfine splitting constants of organic radical anions produced by copper isonitrile system are summarized in Table I. The hyperfine splitting constants of m-dinitrobenzene radical anion were tested by computer simulation.

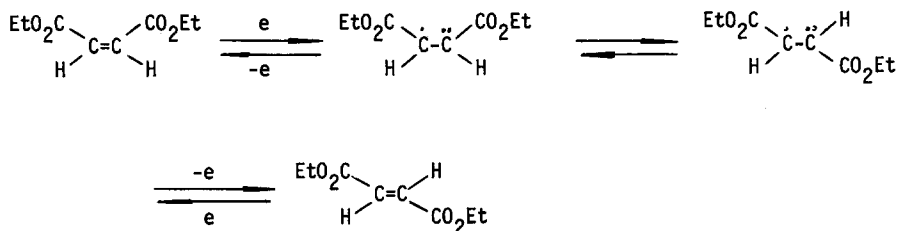
Radical anions prepared by copper isonitrile system seem to be relatively free from the influence of counteraction of copper. ESR spectrum of the m-dinitrobenzene radical anion prepared by copper isonitrile system revealed that two nitro groups on the ring are equivalent to each other. The equivalency of two nitro groups in the m-dinitrobenzene radical anion has been reported also in the electrolytic reduction.⁴ These radical anions are in contrast with the radical anion prepared by the reduction with alkali metal⁵ in a poor coordinating solvent in which two nitro substituents on the benzene ring are not equivalent. It is also to be noted that either metallic copper-isonitrile or Cu_2O -isonitrile produced almost the same ESR spectrum for each of π -substrates in Table I. The characterization of the counter-cations in both cases is the subject of future study.

It has been often found in our synthetic studies utilizing copper-isonitrile system that diethyl maleate undergoes a rapid isomerization to diethyl fumarate under a mild conditions. This isomerization is caused only in the presence of the both components of metallic copper or

Figure 1. ESR spectrum of the m-dinitrobenzene radical anion at room temperature.

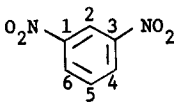
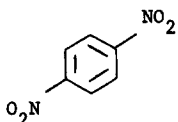
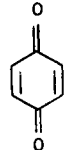
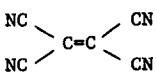


Cu_2O and isonitrile. We would like to propose a reaction mechanism via radical anion for the isomerization.⁶



Esr detection of radical anion from tetracarboethoxyethylene and copper isonitrile may be taken as a support to the above scheme. Cis-trans isomerization of this kind was also observed with 1-phenyl-4,4-dimethyl-penten-1-one-3. This results may be related to a study of House et al.⁷ who have proposed a reaction mechanism involving an electron transfer from cuprate to α,β -unsaturated carbonyl compound for the conjugate addition of lithium dialkylcuprate to α,β -unsaturated carbonyl compound.

Table I
Hyperfine Splitting Constants of Radical Anions.

π -Substrate	Copper compd.	hfsc
	$\text{Cu}/\underline{t}\text{-BuNC}$	$a_{\text{N}} = 3.63$ $a_{\text{H}}^2 = 2.54$ $a_{\text{H}}^5 = 1.12$ $a_{\text{H}}^4 = a_{\text{H}}^6 = 4.89$
	$\text{Cu}_2\text{O}/\underline{t}\text{-BuNC}$	$a_{\text{N}} = 1.18$ $a_{\text{H}} = 1.03$
	$\text{Cu}/\underline{t}\text{-BuNC}$	$a_{\text{H}} = 2.43$
	$\text{Cu}_2\text{O}/\underline{t}\text{-BuNC}$	$a_{\text{N}} = 1.44$

Acknowledgments. We are grateful to Dr. Takashi Kawamura, Department of Hydrocarbon Chemistry, Kyoto University, for the esr measurements and helpful discussions and to Professor Hideki Sakurai and Dr. Mitsuo Kira, Department of Chemistry, Tohoku University, for the computer simulation of esr spectrum of m-dinitrobenzene radical anion.

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