

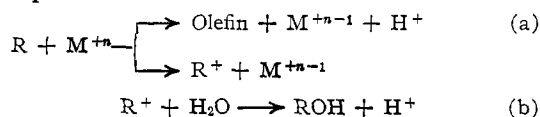
COMMUNICATIONS TO THE EDITOR

THE OXIDATION OF FREE RADICALS BY METAL IONS

Sir:

The effects of metal ions on free radicals have been delineated as reactions involving the modification of free radical activity¹ and oxidation-reduction.² Ligand transfer³ as a mode of an oxidation-reduction reaction has been described recently.^{2,4} We wish to report here some oxidation-reduction reactions which occur by electron transfer rather than ligand transfer.

The electron transfer mechanism for the oxidation of free radicals by metal ions is described by the equations



The distribution of the oxidation products between R^+ (solvolytic products) and olefin is dependent on the structure of the alkyl radical. Table I shows the oxidation of the simple alkyl radicals by cupric ion in aqueous solution to olefinic and alcoholic products.

TABLE I

PRODUCTS FROM THE OXIDATION OF ALKYL RADICALS BY CUPRIC SULFATE

Radical	Cupric ion, M	Olefin, %	Alcohol, %	ΔH_f° (kcal./mole)
Methyl ^b	0.05	0	81	262
Ethyl ^b	.05	48	39	224
	.50	59	28	
<i>sec</i> -Butyl ^c	.05	19 ^d	65	180
<i>tert</i> -Butyl ^e	.05	9	82	166
Allylic ^e	.05	0	85	218

^a Heat of formation of the gaseous ion. ^b From *tert*-alkyl hydroperoxide and Ti^{+3} . ^c From photolysis of methyl ketone. ^d 24% *cis* and 76% *trans*-butene-2. ^e From *tert*-butoxy and butadiene.

In general there is a correlation between the heat of formation of the gaseous ion⁵ and the ease of oxidation of the radical to alcohol by cupric ion.⁶ The exception is the allyl radical whose anomaly is probably attributable to the different solvation requirements of the resonance stabilized carbo-

(1) J. Kochi and F. Rust, *J. Am. Chem. Soc.*, **83**, 2017 (1961).

(2) J. Kochi, *ibid.*, **78**, 4815 (1956); **79**, 2942 (1957). J. Kumamoto, H. De La Mare and F. Rust, *ibid.*, **82**, 1935 (1960).

(3) H. Taube, "Advances in Inorganic Chemistry and Radiochemistry," Editors, H. Emeleus and A. Sharpe, Academic Press, New York, N. Y., 1959, Chap. I.

(4) C. Bamford, A. Jenkins and R. Johnston, *Proc. Royal Soc.*, **A239**, 214 (1957).

(5) F. Field and J. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

(6) The implication is that the olefin is formed from the radical by a synchronous process involving electron transfer and loss of the β -proton.

nium ion compared to its saturated counterparts. Although it is possible in some cases that the solvolytic product arises *via* a ligand transfer process at present, we prefer the alternative two-step mechanism involving electron transfer and then solvation of the carbonium ion, especially with the allylic systems.

The oxidation of alkyl radicals by cupric ions is demonstrated by the preparative reactions. 1-Methyl cyclohexyl hydroperoxide reacts with ferrous sulfate⁷ in the presence of cupric sulfate to form 6-hepten-2-one in 95% yield. Tetrahydropyranyl-2-hydroperoxide reacts⁸ under similar conditions to form 3-buten-1-ol in approximately 20% yield. The cyclohexanone-hydrogen peroxide adduct⁹ is oxidized by the ferrous-cupric couple to 5-hexenoic acid in 76% yield.

Acyl radicals are quantitatively oxidized to carboxylic acid derivatives.¹⁰ Biacetyl is photolyzed in the presence of 0.05 M cupric ions to produce acetic acid quantitatively. In methanol methyl acetate is the exclusive product. Acetone similarly is oxidized to acetic acid and methanol. In neither case is carbon monoxide a product.

(7) E. Hawkins and D. Young, *J. Chem. Soc.*, 2804 (1950).

(8) N. Milas, R. Peeler and O. Mageli, *J. Am. Chem. Soc.*, **76**, 2322 (1954).

(9) M. Kharasch and G. Sosnovsky, *J. Org. Chem.*, **23**, 1362 (1958).

(10) D. Coffman, R. Cramer and W. Mochel, *J. Am. Chem. Soc.*, **80**, 2883 (1958).

SHELL DEVELOPMENT COMPANY
EMERYVILLE RESEARCH CENTER
EMERYVILLE, CALIFORNIA

H. E. DE LA MARE
J. K. KOCHI
F. F. RUST

RECEIVED FEBRUARY 27, 1961

ON A TRANSANNULAR PHOTODESMOTIC TRANSITION¹

Sir:

We wish to report the use of solvent effects to identify a transannular electronic transition involving a carbon-carbon double bond and a carbonyl group. We further suggest that such transitions, which lead to a bond in the excited state between atoms not bonded in the ground state, be called *photodesmotic* (from the Greek, $\phi\omega\tau\omicron\delta\epsilon\sigma\mu\omicron\varsigma$, link caused by light).² In many cases, photodesmotic transitions will be intramolecular charge-transfer transitions,³ but exceptions will exist when the two groups are equivalent.⁴ The present case, *trans*-5-cyclodecenone, is typical of those in which the transition in question is located close to 2000 Å., and therefore near the absorption positions

(1) This communication may be considered as "Effect of Solvent on Spectra. VIII."

(2) We thank Professor H. M. Howe, Classics Department, for his advice in this matter.

(3) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959).

(4) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan *J. Am. Chem. Soc.*, **82**, 5450 (1960).