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Communications

One-electron Reduction of Verdazyl Salts by Metals

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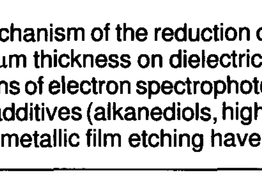
The kinetics and mechanism of the reduction of verdazyl salts by metals (copper, zinc, tin, lead and aluminium), deposited in the form of films of 3–8 μm thickness on dielectric supports of ceramic glass, and by metal alloys in organic solvents, has been investigated by means of electron spectrophotometry and gravimetric analysis; the influence of the metal, medium polarity and the presence of certain additives (alkanediols, highly-dispersed silicon dioxide) upon the reaction kinetics has been established and as a result systems for metallic film etching have been developed.

The investigation of the process of organic electron acceptor one-electron interaction with inorganic reagents (metals) may be useful for clearing up hidden details in organometallic compound formation. In earlier work the reduction of phenoxyl radicals [1] and *ortho*-quinones[2–4] by some alkali and other metals was investigated by means of electron paramagnetic resonance and gravimetric analysis. It was confirmed that one-electron transfer from metal to acceptor took place. However, the above-mentioned work was mainly qualitative except for work on reactions of alkali metals.

In this communication the interaction of such an electron acceptor as verdazyl salts with metals, deposited in the form of films on dielectric supports of ceramic glass and tin–lead alloy POS–60 (containing 60% tin and 40% lead) in organic solvents has been investigated by means of electron spectrophotometry and gravimetric analysis.



A

Ar = Ph, p-NO_2-C_6H_4, p-Cl-C_6H_4
X^- = Br^-, ClO_4^-

Verdazyl salts of general formula **A** were prepared according to the literature method[5] by treating the appropriate verdazyl radical solution with bromine in benzene solution or by an aqueous solution of perchloric acid. Acetonitrile, methanol and ethanol were used as solvents. Electron absorption spectra of the solutions were recorded using a SPECORD M–40 spectrophotometer in silica tubes with a layer 1 cm thick. The point of total metal film etching from the surface of the support was determined visually.

The interaction of verdazyl salt solutions with copper, zinc, tin, lead and aluminium changes the colour of this solution from crimson to bright green, accompanied by a decrease in the absorption band attributed to the verdazyl cation with $\lambda_{max} = 545$ nm and the appearance of two new bands with $\lambda_{max} = 401$ and 715 nm attributed to verdazyl radicals (ref. 6). In electron spectra isobestic points were observed. This fact confirms the assumption that verdazyl salts undergo transformations into products without the formation of any intermediate stable compounds, *i.e.* the reaction equation depends on the stoichiometric ratio of the reagents. The verdazyl salts did not react with iron, nickel and chromium films to quite the same extent.

The experimental data on verdazyl salt molar concentration changes in solution with temperature change from 20–60 °C, obtained according to changes in the absorption band at $\lambda_{max} = 545$ nm, were treated as a time function of interaction with metal according to first-order kinetics. The data were shown graphically to be consistent with first-order kinetics. The effective oxidation rate constants (Table 1) on moving from copper to lead decrease, but the values of the activation energy

Table 1 Kinetics and activation data for interaction of triphenylverdazyl bromide with metal films in organic solvents.

Metal	Acetonitrile		Methanol		Ethanol
	$k^{293}_{eff.}$/ $10^{-3}s^{-1}$	E_a/ kJ mol^{-1}	$\Delta S^{\ddagger}$ /J $mol^{-1}K^{-1}$	$k^{293}_{eff.}$/ $10^{-3}s^{-1}$	$k^{293}_{eff.}$/ $10^{-3}s^{-1}$
Copper	5.82	22	−30	0.75	1.20
Zinc	4.15	24	−21	1.80	0.70
Aluminium	2.30	26	−17	2.10	1.40
Tin	0.82	29	− 9	0.12	0.06
Lead	0.73	31	− 4	0.11	0.08

Table 2 Results on metal film and alloy POS–60 etching by verdazyl salts. The concentration of components (% by weight) was verdazyl salts, 0.015; ethyleneglycol, 10.0; silica A–380, 0.56; solvent, acetonitrile. The surface area of all samples was 7.2 cm^2.

Verdazyl salt	Metal or alloy	Etching rate /g m^{-2} h^{-1}	Time for total etching of the film/min
Triphenylverdazyl bromide	Copper	0.98	5
	Zinc	0.59	9
	Aluminium	0.28	12
	Tin	0.06	16
	Lead	0.05	18
	POS–60 alloy	0.07	—
Tri(*p*-nitrophenyl)-verdazyl bromide	Copper	1.12	3
Tri(*p*-chlorophenyl)-verdazyl chlorate	Copper	1.04	4

increase at the same time, being associated with activation entropies. This confirms the affinity of the oxidation mechanism for all metals. Assuming that the activity of metals as electron donors is determined by their redox potentials, one may expect a reverse trend in reaction rate constants on moving from copper to lead, as well as the reduction of verdazyl salts by iron, nickel and chromium, since their redox potentials are lower than those for copper, lead and tin. However, one-electron oxidation of iron, nickel and chromium did not take place.

The metal structure, bond strength of atoms in the crystal grating and nature of solvents probably has an influence on the reaction rate as well as the redox potential. The interaction of verdazyl salts with copper is therefore more intensive compared to that with zinc, tin, lead or aluminium. The above-mentioned phenomenon may be explained by the formation of copper(I) complexes with acetonitrile.[7]

The increase in oxidation rate of metal films by verdazyl salts was also observed when highly-dispersed silicon dioxide was added to the reaction mixture. The addition of silica (trade name A–380, specific surface 380 m^2 g^{-1}), to the extent of 0.56% by weight, increases the rate of volume loss of the copper film by one order of magnitude.

As a result of this work, systems for metallic film etching have been developed.[8] They make it possible to carry out the process under mild conditions. The results obtained are given in Table 2. The compositions obtained do not contain active components (acids, alkalis or peroxides), and permit etching without destruction of the dielectric support. This allows for the separate etching of metals. The absence of unhealthy gaseous compounds and the possibility of regeneration of initial components allows the creation of reversible technological cycles, which do not bring about pollution by the etching products.

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