

TABLE III
DEVIATIONS OF ATOMS IN COPPER TETRAPHENYLPORPHINE FROM THE PLANE PARALLEL TO THE 001 PLANE AND PASSING THROUGH THE ORIGIN

Atom	Deviation in Å.
Cu	0.00
N	.04
C ₁	.26
C ₂	.24
C ₃	-.09
C ₄	-.24
C ₅	-.42
C ₆	-.76
C ₇	-1.42

The bond distances in the copper tetraphenylporphine and nickel etioporphyrin I² agree to within the experimental errors. Both molecules have a non-planar configuration of the porphyrin ring although the details of the non-planarity are different for the two molecules. The X-ray analysis of palladium tetraphenylporphine, which is isomorphous with copper tetraphenylporphine, is in progress, and both structures will be published in detail at a future time.

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VALENCE EXHIBITED BY ZINC AMALGAM ANODICALLY DISSOLVING IN NITRATE SOLUTIONS¹

Sir:

Sorenson, Davidson and Kleinberg² have proposed that zinc and cadmium dissolve anodically in certain oxidizing agents (chlorates and nitrates) with an initial mean valence between one and two. Other investigators³⁻⁶ have reported the anodic disintegration of such metals as Be, Mg, Al and Fe in salt solutions. In the case of Be and Mg "chunks" of metal have been obtained as a residue and shown to have originated from the electrode and not through nucleation.^{3,7} Therefore, any material dissolving in the electrolyte and not a part of the electrical circuit would not contribute to the faradaic current, and could account for apparent valencies of less than two. The presence of atomic aggregates of colloidal and sub-colloidal size also could account for the reducing properties of the anolyte.

In July, 1962, Dr. T. P. Hoar (Cambridge, England) suggested that the mechanism of anodic dissolution of zinc be studied by the use of a zinc amalgam electrode. The amalgamation would prevent the disintegration of the electrode and the formation of films such as are observed on pure zinc (99.99%) electrodes in nitrate solutions. As the diffusion of zinc ions of any valence would not be prevented by the amalgamation, one would expect the behavior of zinc amalgam to correspond to that of zinc in the same electrolyte as regards the initial mean valence.

(1) This work supported by a research grant from ONR.

(2) D. T. Sorenson, A. W. Davidson and J. Kleinberg, *J. Inorg. Nucl. Chem.*, **13**, 64 (1960).

(3) M. E. Straumanis and D. C. Mathis, *J. Electrochem. Soc.*, **109**, 434 (1962); *J. Less-Common Metals*, **4**, 213 (1962).

(4) W. J. James, M. E. Straumanis, B. K. Bhatia and J. W. Johnson, *J. Electrochem. Soc.*, **109**, 199C (1962).

(5) B. Roald and M. A. Streicher, *ibid.*, **97**, 283 (1950).

(6) G. A. Marsh and E. Schaschl, *ibid.*, **107**, 960 (1960).

(7) M. E. Straumanis and B. K. Bhatia, *ibid.*, **110** (1963).

Accordingly, zinc electrodes were electrolyzed in 3% potassium chloride and in 3% potassium sulfate at 25° employing a current density of 60 ma. cm.⁻². The results confirm the studies of Sorenson, *et al.*, that anodic dissolution in non-oxidizing electrolytes involves only the formation of bivalent ions. Anodic dissolution of zinc in 3% potassium nitrate at 25 and 58° results in valences of less than two (1.82-1.87 at 25°) considerably outside of experimental errors. This is in harmony with results obtained by Sorenson, *et al.*, for zinc dissolving in sodium nitrate.

However, when zinc amalgam is electrolyzed at 60 ma. cm.⁻² in nitrate solution, there is no evidence of univalent ions; the agreement between the faradaic equivalent obtained from the current based on bivalent ions compares excellently with the amount of zinc dissolved as determined by titration with EDTA, and confirmed by weight measurements of the electrode (Table I).

TABLE I

Wt. zinc (calcd.), g.	Wt. zinc (exptl.), g.	Temp., °C.	Apparent valence
0.1262	0.1269	25 ± 0.2	1.99
.1939	.1951	25	1.99
.2851	.2817	25	2.02
.2864	.2734	58	2.09
.0892	.0903	58	1.98

No mercury was detected in solution. A loosely adhering black film was observed on the zinc anode during electrolysis in potassium nitrate but was not present on the amalgam or on zinc in other electrolytes (sulfate and chloride).

The value of 2.09 is higher than normal experimental error can account for and suggests the possibility of a competing electrolytic anode reaction which might conceivably compensate for a decrease in apparent valence arising from non-electrolytic oxidation of univalent zinc ion by the electrolyte. However, the only possible competing electrolytic oxidation would require oxygen evolution and no evolution was observed at the anode. Furthermore, no nitrite ion was detectable in the anolyte after prolonged electrolysis.

The results clearly show, inasmuch as the concept of uncommon valence states is inadequate to explain the anodic dissolution of zinc in oxidizing electrolytes, that mechanisms involving breakdown of the anode into atoms and/or atomic aggregates cannot be rejected.

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SOME CHARGE-TRANSFER SALTS OF 1,2,3,4,5-PENTACARBOMETHOXYCYCLOPENTADIENYL ANION

Sir:

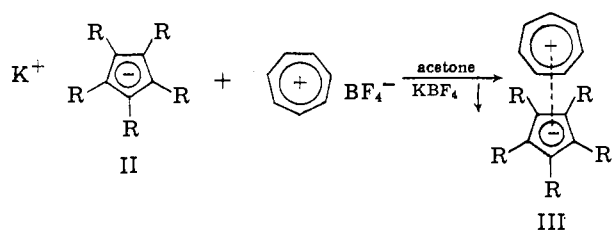
In the course of studying the chemistry of 1,2,3,4,5-pentacarbomethoxycyclopentadiene¹ we found that its anion, I, will function as a planar donor in a series of organic charge-transfer salts, in which the isoelectronic planar cations tropylium, 2,4,6-trimethylpyrylium, pentaphenylpyrylium, N-methylpyridinium and N-methylquinolinium serve as acceptors. Good yields of these stable salts² are obtained by stirring a suspen-

(1) O. Diels, *Ber.*, **75**, 1452 (1942).

(2) Salt formation no doubt is a result of the low nucleophilicity of I. Less substituted cyclopentadienyl anions (thus, less delocalization of the negative charge) have been shown to form covalent compounds with tropylium,³ pyrylium⁴ and pyridium.⁵

(3) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956); M. E. Vol'pin, I. S. Akhrem and D. N. Kursanov, *Zh. Obshch. Khim.*, **28**, 330 (1958); K. Hafner, *Angew. Chem.*, **75**, 43 (1963).

sion of potassium 1,2,3,4,5-pentacarbomethoxycyclopentadienyliide, II,⁶ with an "ylium" salt in an appropriate solvent (*e.g.*, II and tropylium tetrafluoroborate in acetone), separating the inorganic potassium salt (quantitative in all cases), then isolating and recrystallizing the organic salt. Physical properties of



each salt are shown in Table I.

TABLE I
PHYSICAL PROPERTIES OF THE SALTS OF 1,2,3,4,5-PENTACARBOMETHOXYCYCLOPENTADIENE

Cation (m. p. of salt) ^a	Charge-transfer absorptions λ_{max} m μ (ϵ) ^b [color]	N.m.r. spectra τ (multiplicity) ^c assignment ^d
 157-159°(vac) III	470 (1870) [orange]	1.76 (S) C ₇ ⁺ protons 6.41 (S) O—CH ₃
 154-155° IV	418 (758) [yellow]	3.05 (S) =C—H 6.37 (S) O—CH ₃ 7.51 (S) 2,6-CH ₃ 7.72 (S) 4-CH ₃
 250-251° V	420 (17,000) [yellow]	2.25-3.10 (M) =C—H 6.41 (S) O—CH ₃
 104-105° VI	350 (768) [pale yellow]	1.9-2.8 (M) =C—H 6.06 (S) N—CH ₃ 6.34 (S) O—CH ₃
 106-107° VII	402 (1020) [yellow]	1.3-2.8 (M) =C—H 5.82 (S) N—CH ₃ 6.41 (S) O—CH ₃

^a Melting points are corrected. ^b ϵ values were found to be somewhat concentration dependent. ^c S = singlet, M = complex multiplet. ^d Integrations consistent with assignments.

The structure of each salt is established by its analysis, infrared and proton magnetic resonance spectrum.⁷ The ultraviolet-visible spectra appear to be

(4) K. Hafner, *Angew. Chem.*, **69**, 393 (1957).

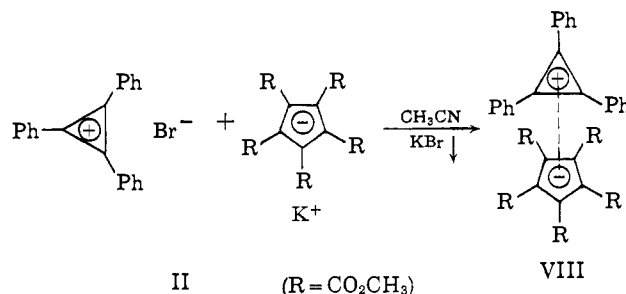
(5) K. Hafner, *Ann.*, **606**, 79 (1957).

(6) The preparation and properties of this compound are described in a paper submitted to *J. Org. Chem.* by the authors.

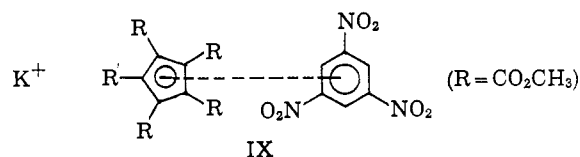
(7) Satisfactory analyses were obtained from various commercial laboratories; infrared spectra were taken in solution (HCCl₃); n.m.r. spectra were recorded with a Varian A-60 spectrometer using chloroform-*d* as solvent and tetramethylsilane as internal standard; ultraviolet-visible spectra were taken with dichloromethane solutions.

composed of the absorptions of the individual ions plus a new long wave length absorption. That this long wave length arises from a charge-transfer transition is shown by a plot of the long wave length absorption frequencies of the cyclopentadienyliide salts III, IV, V, VI and VII against the charge-transfer absorptions of the corresponding iodides.⁸ A nearly linear plot is obtained with a slope of approximately unity.

Yellow acetonitrile solutions of triphenylcyclopropenyl salt, VIII, (identified by n.m.r. and ultraviolet-visible spectra) are readily obtained; however, this salt could not be induced to crystallize. VIII also appears to be of the charge-transfer type (long tailing of broad absorptions from 300 m μ to 500 m μ).⁹



The potassium salt II also forms charge-transfer salts with neutral acceptors. Thus, II and 1,3,5-trinitrobenzene afford the yellow crystalline salt, IX, m.p. 200-201°, II and trinitrofluorenone give a red crystalline salt, m.p. 199-200°, while II and tetracyanoethylene yield an unstable (in solution) blue complex ($\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 590 m μ).



(8) M. Feldman and S. Winstein, *Tetrahedron Letters*, 853 (1962).

(9) We have found that triphenylcyclopropenyl iodide, a yellow salt, has an absorption band at 361 m μ (CH₃CN), an absorption not found in the bromide. We believe this absorption is caused by a charge-transfer transition. This would place the charge-transfer absorption of VIII in the vicinity of 300 m μ , a portion of the spectrum where both triphenylcyclopropenyl cation (307, 320 m μ)¹⁰ and pentacarbomethoxycyclopentadienyliide anion (294 m μ)¹¹ absorb strongly.

(10) R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958).

(11) R. C. Cookson, J. Hudec and B. Whitear, *Proc. Chem. Soc.*, 117 (1961).

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MECHANISM OF THE PHOTOCHEMICAL FORMATION OF PHENANTHRENE FROM *cis*-STILBENE IN THE VAPOR PHASE

Sir:

In an attempt to study the mechanism of the formation of phenanthrene from the photolysis of *cis*-stilbene, we have investigated this system in the vapor phase at 170° at a pressure of about 5 mm. Under these conditions, at both 3130 Å. and shorter wave lengths, photolysis of *cis*-stilbene led to the formation of phenanthrene and hydrogen in equivalent amounts (within experimental error) and *trans*-stilbene. This is in sharp contrast to the recent report¹ that in cyclohexane solution photolysis of *cis*-stilbene leads to phenanthrene only in the presence of oxygen. To reconcile the data in the two phases we have carried out a number of control experiments with the following results.

(1) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist and M. L. Savitz, *J. Am. Chem. Soc.*, **84**, 4361 (1962).