

also contain *p,p'*-DDT. However, these levels are too low to account for the disproportionate ratios.

In Table II are presented the results of an experiment where the exposure to *o,p*-DDT was repeated at a lower level and for a shorter time. While the excess *p,p'*- over the *o,p*-DDT is smaller under these conditions (approximately 2:1), the possible contribution from diet residuals has been reduced about tenfold. Here it is even more apparent that the explanation for the findings in both experiments cannot be attributed to the presence of contaminating sources of *p,p'*-DDT in the control diets.

In order to confirm that the *p,p'*-DDT found in fat by gas chromatography and presumed to originate from *o,p*-DDT is, in fact, *p,p'*-DDT, independent identification was made by micro infrared spectroscopy. The infrared spectrum of *p,p'*-DDT derived from fat was compared with a standard crystalline preparation of *p,p'*-DDT. Precise correspondence of the strong bands at 9.15, 9.85, 12.80, and 13.05  $\mu$  and the medium strength bands at 11.80 and 11.95  $\mu$  was observed. These bands are characteristic of the *para,para'* isomer of DDT. Comparison with a standard crystalline preparation of *o,p*-DDT showed that the bands at 9.51 and 9.62  $\mu$  characteristic for this isomer were absent.

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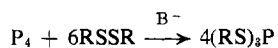
## Organic Phosphorus-Sulfur Chemistry.

### I. A Novel Synthesis of Tertiary Trithiophosphites

Sir:

Trialkyl trithiophosphites have been prepared by the interaction of yellow phosphorus and dialkyl disulfides at 170–210°. Since homolysis of disulfides occurs at these temperatures,<sup>2</sup> the reaction presumably involves free radicals.

We wish to report an ionic reaction of yellow phosphorus with organic disulfides in a dipolar aprotic



solvent. Unlike the thermal process,<sup>1</sup> which requires extended reaction time and often superatmospheric pressures, the new reaction proceeds exceptionally smoothly under very mild conditions. A general procedure is as follows. About 1 ml. of 15 *N* potassium hydroxide is added to a stirred mixture of 1 g.-atom of finely divided phosphorus and 1.5 moles of disulfide in 500 ml. of acetone at room temperature under nitrogen. The reaction is slightly exothermic and is usually complete within 30 min. The product is isolated by vacuum distillation in greater than 90% yield. If yellow phosphorus is present in excess, dark solids having high phosphorus content are formed at the end of the reac-

(1) D. R. Stevens and R. S. Spindt, U. S. Patent 2,542,370 (1951); G. D. McLeod, U. S. Patent 2,768,194 (1956); G. D. McLeod and E. L. d'Ouville, U. S. Patent 2,819,290 (1958).

(2) For a summary of the evidence, see W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y. 1962, pp. 42–45.

tion in addition to the trithiophosphite. The reaction may be carried out more conveniently by using molten phosphorus (m.p. 44°). The reaction is generally applicable to simple aliphatic and aromatic disulfides.

Group I-A bases such as hydroxides, alkoxides, mercaptides, alkyls, amides, hydrides, and phosphides are effective catalysts. Grignard reagents and calcium amide may also be used as catalysts. The reaction is rapid in dipolar aprotic solvents such as acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide; but it proceeds extremely slowly in protic solvents such as methanol or in ethereal solvents such as tetrahydrofuran.

Data indicate that the reaction most probably involves bimolecular nucleophilic substitutions at phosphorus and at sulfur. The detailed mechanism is necessarily complex, since all of the six P–P bonds in the P<sub>4</sub> tetrahedron must be progressively cleaved, with each cleavage producing at least one new organophosphorus intermediate.

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### About the Ahrland-Chat-Davies Classification of Rhodium and Iridium into Type (a) or (b) Central Atoms

Sir:

The Ahrland-Chat-Davies<sup>1</sup> classification of the elements and ions according to their relative affinities for ligands, together with Pearson's<sup>2</sup> generalization that hard (type (a)) acids prefer to associate with hard bases, and soft (type (b)) acids prefer soft bases, has proved to be a useful tool for explaining or predicting the stability of compounds. For elements on the border line where it is not possible to assign hardness or softness unambiguously, several explanations can be found as to why an atom or ion sometimes exhibits hard and sometimes soft character. These include the ionization state,<sup>3</sup> the steric factor,<sup>4</sup> and the nature of other ligands in the complex.<sup>3,5</sup>

Ahrland, Chat, and Davies<sup>1</sup> classify rhodium as a type (b) element, but close to the border line of type (a), and iridium as class (b). Pearson<sup>2</sup> does not classify rhodium, and derives for iridium(III) class (a) behavior on the basis of equilibrium data<sup>6</sup> for the hydrolysis of [Ir(NH<sub>3</sub>)<sub>5</sub>X]<sup>2+</sup>, where X refers to a halide ion.

Thiocyanate when coordinated to these metals may serve as a test case for this classification since this anion is known to be a difunctional ligand which can be attached to the metal cation either through the soft sulfur or the hard nitrogen atom. This property together with Pearson's rule that hard acids prefer hard bases and soft acids prefer soft bases facilitates the description of these central atoms as relatively more hard or

(1) S. Ahrland, J. Chat, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

(2) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(3) C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964).

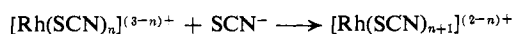
(4) F. Basolo, W. H. Baddley, and J. L. Burmeister, *ibid.*, **3**, 1202 (1964).

(5) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

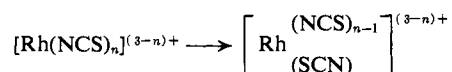
(6) A. B. Lamb and L. T. Fairhall, *J. Am. Chem. Soc.*, **45**, 378 (1923).

soft. We succeeded in preparing the two linkage isomers of thiocyanatopentaamminerhodium(III) and -iridium(III) by refluxing the aquopentaammines with an excess of NaSCN in aqueous solution. The characterization of the compounds and their assignments are given below. By far the largest part (~60–70%) of the yielded product represents the nitrogen-bonded isomer (isothiocyanate). The other components are formed only in small yields (some 10%). Prolonged boiling of the reaction mixture decreases the yield of the sulfur-bonded (thiocyanate) complexes. Already from this relation we may conclude that the nitrogen-bonded isomers are the more stable components. Kinetic experiments performed at 40° indicate negligible conversion of the two isomers into each other after 48 hr., but an appreciable rearrangement of the sulfur-bonded Rh isomer into the nitrogen-bonded component can be observed after 3 hr. at 78°. However, the reaction cannot be followed completely since decomposition products are formed. The first-order rate constant for this reaction calculated for the first 50 hr. is  $k = 2.7 \times 10^{-6} \text{ sec.}^{-1}$ . The nitrogen-bonded Rh complex, on the other hand, does not show any tendency for isomerization at 78° but yields distinct decomposition products even after 24 hr. Addition of alcohol does not accelerate the attainment of the equilibrium but facilitates the formation of decomposition products.

These experiments apparently confirm the class (a) behavior of the radicals  $[\text{Rh}(\text{NH}_3)_5]^{3+}$  and  $[\text{Ir}(\text{NH}_3)_5]^{3+}$ , but do not enable the classification of the free ions. The softness of the bare ions is suggested by the observation that all the thiocyanate ligands in  $[\text{Rh}(\text{SCN})_6]^{3-}$  are bonded through the sulfur.<sup>7,8</sup> If in the reaction



series the first  $\text{SCN}^-$  ( $n = 0$ ) is bonded through the sulfur atom, all the other  $\text{SCN}^-$  ( $n = 1$  to 5) also enter through sulfur, since each additional ligand makes the central atom site softer. In this case, class (b) character is obvious for free  $\text{Rh}^{3+}$ . On the other hand, class (a) character would be deduced if the first  $\text{SCN}^-$  ( $n = 0$ ) were bonded through nitrogen. In this case we distinguish between two possibilities. If N-coordinated  $\text{NCS}^-$  made the Rh site harder, then the linkage properties of  $[\text{Rh}(\text{SCN})_6]^{3-}$  could not be explained. The other more improbable case is that the Rh site gets softer upon coordination through the nitrogen atom. Then at a certain  $n$ , a rearrangement process



has to take place. This reaction or some other one may think of can only go through a bimolecular path, since the species  $[\text{Rh}(\text{NCS})_{n-1}]$  appearing in a monomolecular process was assumed to be hard in the reaction series. Rearrangement reactions of this kind, however, are observed to have monomolecular paths.<sup>9,10</sup> The above arguments still hold in solution when the other ligand sites are occupied by hard solvent molecules (e.g.,  $\text{H}_2\text{O}$ ). Further evidence for the softness of  $\text{Rh}^{3+}$  and  $\text{Ir}^{3+}$  is the high insolubility of their iodides compared with their chlorides and bromides. Solubil-

ity arguments can be employed when solvation effects are neglected. As for rhodium, we would rather suggest softness for iridium, following the usual trend within a group of the periodic table.<sup>1</sup> For lower oxidation states an even softer behavior is expected.

The characterization and assignment of the acidopentaammines by spectroscopic investigations are given in Tables I and II.

Table I. Visible and Ultraviolet Spectra<sup>a</sup>

$\lambda, \text{m}\mu$	$\epsilon$	$\lambda, \text{m}\mu$	$\epsilon$
N-Bonded Rh Isomer		S-Bonded Rh Isomer	
320	460	375	85
(240)	2200	323	220
(215)	5100	(280)	450
		233	19,200
N-Bonded Ir Isomer		S-Bonded Ir Isomer	
(330)	64	(355)	35
(260)	550	(310)	100
(230)	2000	(275)	180

<sup>a</sup> Band maxima in  $\text{m}\mu$  and molar extinction coefficients  $\epsilon$  (band shoulders in brackets). The assignments in Table I are made according to the spectrochemical series.<sup>11</sup>

Table II. Infrared Spectra<sup>a</sup>

N-Bonded Rh Isomer	S-Bonded Rh Isomer
C–N stretch, 2145 (s, b)	2115 (s, sp)
C–S stretch, 815 (s)	730 (w, b)
N-Bonded Ir Isomer	S-Bonded Ir Isomer
C–N stretch, 2140 (s, b)	2110 (s, sp)
C–S stretch, 825 (s)	700 (m)

<sup>a</sup> Fundamental frequencies in  $\text{cm.}^{-1}$  of the SCN group of samples in KBr disks. Abbreviations: s, strong; m, medium; w, weak; b, broad; sp, sharp.

According to Turco and Pecile<sup>5</sup> and Tramer,<sup>12</sup> only the position of the C–S stretching frequency can serve as a criterion for the assignment of the two linkage isomers. The bands found are actually in the region given by these authors being characteristic of the two isomers.

(11) See C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962.

(12) A. Tramer, *J. chim. phys.*, **59**, 232 (1962).

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## Anionic Oxidation of Simple Alkyl Aromatics

Sir:

Although the base-catalyzed oxidation of hydrocarbon and related materials has received considerable attention by Russell,<sup>1</sup> the compounds studied were necessarily of a group possessing a readily ionized C–H bond. This restriction was imposed by the presence of dimethyl sulfoxide which itself is reactive with molecular oxygen unless it is diluted with considerable proportions

(7) Z. V. Zvonkova, *Zh. Fiz. Khim.*, **27**, 100 (1953).

(8) H.-H. Schmidtke, *Z. physik. Chem.* (Frankfurt), **40**, 96 (1964).

(9) F. Basolo and G. S. Hamaker, *Inorg. Chem.*, **1**, 1 (1962).

(10) J. L. Burmeister and F. Basolo, *ibid.*, **3**, 1587 (1964).

(1) G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954); G. A. Russell, E. G. Jansen, H. D. Becker, and F. Smentkowski, *ibid.*, **84**, 2652 (1962); G. A. Russell, A. J. Moye, and K. Nagpal, *ibid.*, **84**, 4154 (1962).