TABLE II

GAS PHASE ULTRAVIOLET ABSORPTION MAXIMA, Å. (ϵ)

$C_2P_2(CF_3)_4$ (I)	$C_2P_3(CF_3)_5$ (II)	$H_2(CF_3P)_2$[6]	$H_2(CF_3P)_3$[6]
2480 (2300)	2750 (3600)	2040 (7400)	2240 (5500)
2150 (4500)	2120 (9200)		2075 (7600)
2000 (8400)			

We had earlier argued that the (formally) nonbonding electron pair on each phosphorus atom in polyphosphines was delocalized in π-type orbitals.[6] This concept receives further support from the observation that the heterocyclic polyphosphines absorb ultraviolet light at longer wave length than the corresponding open-chain di- and triphosphine (Table II). This clearly suggests that the orbitals of the polyphosphine portion of the ring overlap with the carbon–carbon π-orbitals.

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Photoisomerization of Dialkylbenzenes[1]

Sir:

In previous investigations[2,3] of the products of photolysis of alkylbenzenes attention has been confined to the gaseous and polymerized products. We wish to report that hydrocarbons of intermediate volatility are also formed in significant amounts and particularly that photoisomerization is an important process in the case of dialkylbenzenes.

Some of the products found upon irradiating the vapors of o-xylene, m-xylene, and toluene with mercury arcs are shown in Table I. Volatile products were

TABLE I

VAPOR-PHASE PHOTOLYSIS OF SOME METHYLBENZENES

	o-Xylene		m-Xylene	Toluene
Conditions[a,b]	a	b	b	b
Time, min.	20	60	30	60
Product		Yield, mole %		
H_2	1.52	1.02	0.56	0.28
CH_4	0.31	0.18	0.11	0.08
C_2H_6	0.17	0.10	0.01	0.01
C_6H_6	0.05	0.04	0.004	0.28
$C_6H_5CH_3$	1.24	1.08	0.31	(94.0)
$C_6H_5C_2H_5$	0.04	0.016	0.004	0.19
$C_6H_4(CH_3)_2$				
o-	(74.0)	(81.3)	1.09	0.005
m-	5.44	3.66	(85.5)	0.007
p-	0.49	0.20	4.1	0.003
$C_6H_4(CH_3)C_2H_5$				
o-	0.58	0.48	0.016	
m-	0.11	0.09	0.14	
p-	0.01	0.01	0.07	
"Polymer"	18.0[c]	13.1[c]	8.8[c]	5.3[c]

[a] Irradiated at 35° with a mercury resonance lamp, Nestor and Faust NFUV-300, at a pressure of 6 mm. in an annular quartz vessel of 800 cc. volume. [b] Irradiated at 35° with a high pressure mercury lamp, Hanovia 673-A, at pressures of 5–7 mm. in a 630-cc. Vycor vessel. [c] Weight per cent of products not volatile at room temperature and 10^{-4} mm. pressure.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.
(2) R. R. Hentz and M. Burton, *J. Am. Chem. Soc.*, **73**, 532 (1951).
(3) A. H. Sehon and B. de B. Darwent, *J. Chem. Phys.*, **23**, 822 (1955).

identified and measured by vapor phase chromatography; "polymer" was determined as the difference in weight between the initial sample and recovered material volatile at room temperature and 10^{-4} mm. pressure. In each case the major product is polymer; other important products include hydrogen, methane, and molecules in which a hydrogen atom replaces or is replaced by a methyl group. In the case of the xylenes, the yield of isomeric products is exceeded only by that of polymer. This contrasts sharply with γ-radiolysis[4] where isomeric products are relatively minor products.

The distribution of isomeric xylenes indicates that photoisomerization is a highly selective process. Since only a small proportion of p-xylene is found in the photolyses of o-xylene, and this is completely eliminated at lower conversions, the process cannot involve a 1,3 shift of the methyl group. A 1,2 shift is at least the predominant path in photoisomerization of m-xylene since the yield of o-xylene, which can be formed by either a 1,2 or 1,4 shift, is much less than that of p-xylene.

Quantum yields for isomerization and polymerization in photolysis of o-xylene with the resonance lamp were determined by uranyl oxalate actinometry to be 0.012 and 0.032, respectively. The value for isomerization is in excellent agreement with one of 0.014 ± 0.002 obtained at one-thirtieth the conversion and one-thousandth the intensity using light from a high pressure mercury arc, passed through a monochromator set at 2500 Å., and measured with a calibrated thermopile.

Direct determination of quantum yields for the experiments of Table I with the high pressure arc was not feasible, but they are essentially proportional to the yields of product per unit time, since conditions of illumination were identical and the absorption spectra of the three hydrocarbons are very similar. The quantum yield for isomerization of m-xylene is thus somewhat more than twice that of o-xylene. Based on a value of 0.012 for isomerization of o-xylene, the calculated quantum yields for "gas" and "polymer" from toluene are 0.0010 and 0.015, respectively, about fifteen times those estimated by Hentz and Burton.[2]

The isomerization of m-xylene has also been observed in the liquid phase. The ratio of *ortho* to *para* isomers is essentially the same in the pure liquid, in isohexane solution, and in the vapor; the quantum yield in solution is 0.006, about one-fifth that in the vapor.

The migration of ethyl groups has also been demonstrated. The quantum yield for isomerization of o-diethylbenzene vapor is about twice that for o-xylene.

In order to obtain additional information about the process of photoisomerization, m-xylene has been photolyzed in the presence of foreign gases. The results are summarized in Table II. The ratio of o- to p-xylene produced is relatively constant, suggesting that both isomers are formed from a common precursor. Although radicals are known[5] to be formed by photolysis of xylenes, our results indicate that the isomers are not formed by radical recombination. The fact that ethylene has no effect on the yield excludes participation of hydrogen atoms[6]; the relatively small

(4) K. E. Wilzbach and L. Kaplan, unpublished results.
(5) G. Porter and E. J. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955).
(6) K. Yang, *J. Am. Chem. Soc.*, **84**, 719 (1962).

TABLE II
EFFECT OF FOREIGN GASES ON PHOTOISOMERIZATION OF m-XYLENE[a]

Added gas	None	N_2	O_2	O_2	C_2H_4
Pressure, mm.		100	100	9	2.4
Isomer			Yield, %		
p-	4.10	2.81	0.83	2.16	4.12
o-	1.09	0.81	0.29	0.63	1.14
m- (recovered)	85.5	91.6	84.8	85.4	86.9

[a] Irradiated for 30 min. under condition b of Table I.

effect of oxygen at 9 mm. pressure argues against the participation of methyl radicals.[7] The fact that isomerization is independent of the intensity supports the conclusion that it does not occur by radical recombination and also rules out reactions between excited molecules.

The results of Table II do not permit an unambiguous choice between singlet and triplet as the excited state leading to isomerization, since little is known about the lifetimes of these states in xylene vapor. The inhibition by oxygen, however, appears to be more consistent with a singlet state. It cannot be due simply to collisional deactivation, since the effect of nitrogen at the same pressure is much smaller. The magnitude of the effect with oxygen at 9 mm. is comparable to that observed[8] for quenching of fluorescence in benzene vapor, and oxygen is known[9] to quench the fluorescence of xylene in solution. A much larger inhibition would be expected if a triplet were involved unless it has a lifetime much shorter than that of benzene triplet[8] or is quenched less efficiently by O_2 than the triplets of other aromatic hydrocarbons.[10]

(7) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 2, Reinhold Publishing Corp., New York, N. Y., 1954, p. 612.

(8) H. Ishikawa and W. A. Noyes, Jr., J. Chem. Phys., 37, 583 (1962).

(9) T. V. Ivanova, P. I. Kudryashov, and B. Ya. Sveshnikov, Dokl. Akad. Nauk SSSR, 138, 572 (1961); Soviet Phys., 6, 407 (1961).

(10) G. Porter and M. W. Windsor, Proc. Roy. Soc. (London), A245, 238 (1958).

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The Nature of Vitamin B_{12s}

Sir:

The power of vitamin B_{12s}[1] (hydridocobalamin) as a reductant and the analogy which can be drawn between it and $HCo^{III}(CN)_5^{-3}$ have led to the supposition that this compound may contain a cobalt–hydrogen bond.[2,3] We report herein experiments which cast considerable doubt on this supposition, and which are consistent with the postulation of the cobalt atom itself as the electron acceptor in the reduction of vitamin B_{12} to vitamin B_{12s}. The experimental method consisted in forming B_{12s} in a deuterium-rich medium and testing for incorporation of deuterium as deuteride in the product by examination of the hydrogen produced upon acidification of the product.

Vitamin B_{12s} was produced by reduction of cyanocobalamin (Sigma Chemical Co.) by zinc dust in 10 ml. portions of 99.5% D_2O, after equilibrating the

(1) For a comprehensive review see R. Bonnett, Chem. Rev., 63, 573 (1963).

(2) O. Mueller and G. Mueller, Biochem. Z., 336, 299 (1962).

(3) E. L. Smith, L. Merwyn, A. W. Johnson, and N. Shaw, Nature, 194, 1175 (1962).

TABLE I
DECOMPOSITION OF VITAMIN B_{12s}

Expt.	Cor. wt. of B_{12} taken, mg.	Reduction medium	Vol. of H_2 evolved, STP	$[H_2]/[HD]$
I	49.0	0.02 M NaOD	0.34	140
II	49.0	1% ND_4Cl[a]	0.55	>60
III	49.0	1% ND_4Cl	0.44	30

[a] Five milliliters of 0.48 M NaOD added immediately before filtration.

starting material with D_2O. As the electrolyte in this reduction, warm 0.02 M NaOD served equally as well as the 10% NH_4Cl previously used.[2] The amount of cyanocobalamin taken in these experiments was necessarily small in comparison to the amount of water used. Because the usual isotope effect would favor the production of hydridocobalamin over deuteridocobalamin in this situation, the zinc was left in contact with the starting solutions for at least 24 hr. Thus, the cyclic formation of B_{12s} and its oxidation by water,[4] the side reaction of zinc with water over the long period, and the small ratio of protium to deuterium in the water should have favored formation of deuteridocobalamin, if B_{12s} were indeed a hydride.

After the zinc reduction the solution of B_{12s} was drawn through a sintered glass filter disk into a bulb where it was evaporated to dryness under vacuum. In experiment II (Table I) the solution was made alkaline with 5 ml. of deaerated 0.48 M NaOD before filtering to ensure the stability of the B_{12s} during evaporation. In experiment III this precaution was omitted, and by freezing the solution immediately after transfer and subliming D_2O from the frozen mixture, decomposition of B_{12s} at the pH of ND_4Cl was avoided. The solids left in all experiments had the same color as the B_{12s} solutions.

Pure 0.5 M HCl in H_2O, deaerated by saturation with CO_2, was then added to the solid, whereupon the mixture immediately assumed the brown color of vitamin B_{12r}, and gas was evolved. The gas was freed of condensable material by passage through liquid nitrogen traps and was collected in a gas buret. It was semiquantitatively analyzed by mass spectrometry and found to contain hydrogen with no significant amount of deuterium, as shown in Table I. We attribute the HD formed in these experiments, which represents at most only a few per cent of the reducing power of the B_{12s} on the basis of the amount of hydrogen it yielded, to traces of water of hydration retained in the solid. These results indicate no incorporation of hydrogen as hydride into the vitamin B_{12s} molecule when the latter is formed by reduction with zinc in aqueous solution.

The formulation of vitamin B_{12s} as a compound of cobalt(I) is consistent with the results of these experiments and with its known reactions with electrophilic reagents.[2,5] If, as has been suggested,[6] vitamin B_{12s} consists of an equilibrium mixture of the two forms, $Co^{III}H^-$ and Co^IH^+, the equilibrium must largely favor the Co^IH^+ form, which must also react faster than the hydride; otherwise, we should have found HD rather than hydrogen in the reaction

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(5) A. W. Johnson, L. Mervyn, N. Shaw, and E. L. Smith, J. Chem. Soc., 4146 (1963).

(6) D. Dolphin, A. W. Johnson, R. Rodrigo, and N. Shaw, Pure Appl. Chem., 7, 539 (1963).