By analogy to the above results, the temperaturedependent deactivation of coronene in PMM or DER-332 may be due to thermal activation from T_1 of coronene at 19,700 cm⁻¹ to the lowest triplet state of the plastics. The observed activation energies for triplet deactivation are 4900 and 5800 cm⁻¹. The triplet energy levels for PMM or DER-332 would thus have to be about 25,000 cm⁻¹ to be consistent with thermal deactivation to the matrix. Unfortunately, the phosphorescence spectra of DER-332 and PMM are too diffuse to provide an accurate estimate of the energy levels of the lowest triplet level for DER-332 or PMM. However, the spectra indicate the lowest triplet level is between 23,000 and 26,000 cm⁻¹ for both plastics. Based on this work, it is likely that the plastic host is involved in a part of the temperature-dependent deactivation of coronene. However, the larger values of $k_{P,2}(T)$ obtained for coronene- h_{12} in PMM than for coronene- d_{12} in PMM (Figure 6) indicate that a part of the temperature dependence is intramolecular.

Photochemistry of Metal Aryls in Benzene

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When dilute benzene solutions of the metal perphenyls, $Pb(C_6H_5)_4$, $Sn(C_6H_5)_4$, and $As(C_6H_5)_3$, are irradiated at 2537 A under such conditions that essentially all the energy is absorbed by the benzene, biphenyl is produced. In all cases, at low concentrations the quantum yield of biphenyl, $\Phi((C_6H_5)_2)$, increases markedly with increasing concentration of metal perphenyl; $\Phi((C_6H_5)_2)$ appears to reach limiting values much less than unity at concentrations of the order of 0.01 M. (Some new, rigorously developed data on luminescence quenching, also presented, disagree with previously reported values.) Results are interpreted in terms of energy transfer from excited benzene to the metal perphenyl and are compared with those obtained in studies of luminescence quenching, and of high-energy (${}^{60}Co-\gamma$) sensitized decomposition of the metal perphenyls in benzene. It is concluded on the basis of these comparisons and previous studies that donor states other than the ${}^{1}B_{2u}$ of benzene are also involved in ${}^{60}Co-\gamma$ -sensitized decomposition and that quenching of luminescence by metal perphenyls in benzene solutions may also involve such other states to some small extent.

Introduction

Significant processes in the quenching, by metal perphenyls, of high-energy induced luminescence of organic scintillators in deaerated benzene solutions³ may be summarized as

$$S \longrightarrow S^*$$
 (0)

$$S^* \longrightarrow S$$
 (1)

$$S^* + X \longrightarrow S + X^* \tag{3}$$

$$\mathbf{X}^* \longrightarrow \mathbf{X} + h\nu \tag{6}$$

 $S^* + D \longrightarrow S + D$ (7)

$$S^* + D \longrightarrow S + D^* \tag{8}$$

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The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-531.

⁽³⁾ J. L. Kropp and M. Burton, J. Chem. Phys., 37, 1752 (1962).

$$D^* \longrightarrow \text{products}$$
 (9)

$$D^* \longrightarrow D$$
 (10)

where S, X, and D here refer, respectively, to solvent (or, perhaps more properly, the solution system), scintillator, and quencher. In benzene solutions, the donor state in reaction 3 has been shown⁴ to be the first excited singlet state of benzene, ${}^{1}B_{2u}$. The quenching processes of major interest are those involving deactivation of this state by the quencher (metal perphenyl in this work). Deactivation of excited scintillator by the quencher has been shown to be unimportant in these systems.³

Cobalt-60 γ irradiation of deaerated benzene solutions of metal perphenyls in the absence of scintillators leads to chemical effects which have been interpreted in terms of an energy transfer process such as reaction 8 followed by dissociation of excited metal perphenyl.⁵ In both luminescence quenching and radiation-sensitized decomposition, the ¹B_{2u} state of benzene is a donor state of excitation; however, kinetic study of the two processes showed that in the radiation-sensitized decomposition at least one donor state other than the ¹B_{2u} is involved and that the ¹B_{2u} is a relatively minor contributor. An additional conclusion that only the ¹B_{2u} state of benzene is involved in quenching by heavy-metal perphenyl appears, in the light of this present paper, to be possibly not quite correct.

This report describes the results of studies of ultraviolet irradiation of deaerated benzene solutions of Pb(C₆H₅)₄, Sn(C₆H₅)₄, and As(C₆H₅)₃ at 2537 A. Under the conditions employed, essentially all the incident energy is absorbed by the benzene with production of the ¹B_{2u} state of benzene, the donor state in luminescence. Also, we have reexamined some values for γ_0' , a characteristic luminescence parameter measured and reported in prior work^{1,3,5} (for ⁶⁰Co-initiated processes).

Experimental Section

Methods of purification of chemicals, deaeration of samples, and analysis of products have been described in an earlier paper.⁵

Samples of 5-cc volume were irradiated in cylindrical cells (constructed from 13-mm o.d. Vycor tubing) fitted with magnetically rotated glass stirrers which permitted efficient stirring during irradiation. The light source was a Hanovia 2537-A mercury resonance lamp in the shape of a flat helix. The cell holder had two adjacent positions which permitted simultaneous irradiation of a sample cell and an ethyl iodide actinometer. The quantum yield of iodine for the ethyl iodide actinometer, the intensity employed was about 7×10^{19} quanta l.⁻¹

min⁻¹. In general, the conversion of metal perphenyl was less than 1%.

Results

Irradiation of pure benzene at 2537A yields only trace amounts of biphenyl which make difficult the accurate determination of quantum yield, $\Phi((C_6H_5)_2)$, but the value is certainly less than 10^{-3} . Irradiation of dilute benzene solutions⁷ of the metal perphenyls at 2537 A produces much greater yields of biphenyl; *cf*. Figure 1. In all cases, $\Phi((C_6H_5)_2)$ increases markedly with increasing concentration of metal perphenyl at low concentrations, but approaches a limiting value much less than unity. The isomeric dihydrobiphenyls are also produced, but yields were too small to permit meaningful measurements of quantum yields.

New γ_0' values established for ⁶⁰Co-initiated processes by refinement of previously described technique^{4a} are shown in Table I.

Table I :	Comparison of Significant Kinetic Ratios	
Calculated	from Chemical and Luminescence Effects	

Compound	i/s ^a	k_{8}/k_{1}	70' b
$\frac{\mathrm{Sn}(\mathrm{C}_{6}\mathrm{H}_{5})_{4}}{\mathrm{Pb}(\mathrm{C}_{6}\mathrm{H}_{5})_{4}}$	70 237	776 612	1170 820
$As(C_6H_5)_3$	50	900	1300

^a i/s is defined on an experimental basis as ratio of intercept to slope in a Stern-Volmer plot of $G((C_6H_5)_2)$ presumably resultant from excitation transfer (from ref 5). ^b γ_0' is defined on an experimental basis as the reciprocal of the intercept of a plot of reciprocal Stern-Volmer quenching constants vs. concentration of scintillator (cf. ref 3). New, corrected values of γ_0' for Sb(C₆H₅)₃ and Bi(C₆H₅)₂ are 1000 and 1320, respectively. The five new values replace the corresponding ones given in ref 5.

Discussion

Because essentially all the incident radiation is absorbed by the benzene at the concentrations of metal perphenyls employed, it is concluded that the observed increases in $\Phi((C_6H_5)_2)$ are the result of energy transfer from excited benzene to the metal perphenyl. Presum-

^{(4) (}a) S. Lipsky and M. Burton, J. Chem. Phys., 31, 1221 (1959); (b) S. Lipsky, W. P. Helman, and J. F. Merklin, "Luminescence of Organic and Inorganic Materials," H. P. Kallmann and G. M. Spruch, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter I, p 83.

⁽⁵⁾ D. B. Peterson, T. Arakawa, D. A. G. Walmsley, and M. Burton, J. Phys. Chem., 69, 2880 (1965).

⁽⁶⁾ E. Cochran, W. H. Hamill, and R. R. Williams, Jr., J. Am. Chem. Soc., 76, 2145 (1954).

⁽⁷⁾ The metal perphenyls absorb in the same region as benzene and at 2537 A have absorptivities considerably greater than benzene. However, for the concentrations employed, essentially all of the 2537 A is absorbed by the benzene.



Figure 1. Quantum yields for 2537-A photolysis of metal perphenyls in benzene: O, $Pb(C_6H_5)_4$; O, $As(C_6H_5)_2$; and \bullet , $Sn(C_6H_5)_4$. Values for $Pb(C_6H_5)_4$ correspond to numbers on the right ordinate, whereas values for $As(C_6H_5)_4$ and $Sn(C_6H_5)_4$ correspond to the left ordinate.

ably, biphenyl is produced from phenyl radicals generated by dissociation of the excited metal perphenyl by reactions similar to those involved in high-energy sensitized decomposition.^{5,8}

Excitation of benzene at 2537 A yields initially the ${}^{1}B_{2u}$ state, shown to be the donor state in high-energy induced luminescence for the system benzene-1,6-diphenylhexatriene-phenylbromide.48 Previous studies of the quenching by metal perphenyls³ of such luminescence produced by ${}^{60}Co-\gamma$ excitation were interpreted in terms of energy transfer from the ¹B_{2u} state of benzene to the metal perphenyl. Although this work is in agreement with that interpretation, it should be pointed out that the values for k_8/k_1 , calculated from 2537-A sensitized decomposition (see below), are lower than their corresponding ${}^{60}\text{Co-}\gamma$ luminescence parameters, γ_0' . Hence, in the cases of ⁶⁰Co- γ -excited luminescence, quenching by metal perphenyls appears to proceed not only by energy transfer from the ${}^{1}B_{2u}$ state of benzene but perhaps also, to some extent, by other transfer mechanisms

$$\mathbf{B}^* \longrightarrow \mathbf{B} \tag{1}$$

$$\mathbf{B}^* + \mathbf{M}(\mathbf{C}_6\mathbf{H}_5)_n \longrightarrow \mathbf{M}(\mathbf{C}_6\mathbf{H}_5)_n^* + \mathbf{B}$$
(8)

$$M(C_6H_5)_n^* \longrightarrow M(C_6H_5)_{n-a} + a(C_6H_5)$$
(9)

$$M(C_6H_5)_n^* \longrightarrow M(C_6H_5)_n \tag{10}$$

B^{*} is the first excited singlet state $({}^{1}B_{2u})$ of benzene, and $M(C_{6}H_{5})_{n}^{*}$ is an unspecified excited state of the metal perphenyl. The phenyl radicals generated in reaction 9 yield biphenyl by a reaction sequence which involves benzene itself.^{5,8,9} We have found, in the course of this work, that no biphenyl is produced from solutions of perphenyls in cyclohexane in either photolysis or radiolysis. Thus, benzene must be involved in the biphenyl production here reported.

A simple steady-state treatment of the total mechanism leads to the expression

$$\Phi((C_{6}H_{5})_{2}) = \frac{Ak_{8}[M(C_{6}H_{5})_{n}]}{k_{1} + k_{8}[M(C_{6}H_{5})_{n}]}$$

where $A = fk_9\Phi(\mathbf{B}^*)/(k_9 + k_{10})$. In this notation, $\Phi(\mathbf{B}^*)$ is the quantum yield for the excitation of benzene to the ${}^{1}\mathbf{B}_{2u}$ state and f is a factor expressing the stoichiometric relationship between dissociation of metal perphenyl and production of biphenyl. The k's refer to specific rates of reactions indicated by the subscripts; k_1 is the specific rate for the totality of processes other than reaction 8 by which \mathbf{B}^* returns to the ground state.

Values of k_8/k_1 (which relate to the photosensitized decomposition) were obtained, from the same data indicated in Figure 1, from the ratio of intercept to slope for plots of the reciprocal of $\Phi((C_6H_5)_2)$ vs. the reciprocal of $[M(C_6H_5)_n]$. They can be compared with ratios of i/s obtained independently from studies of high-energy ⁶⁰Co- γ -sensitized decomposition⁵ and with the *new* values of γ_0' obtained independently by a similar treatment of data from studies of luminescence quenching (in the present work). Table I shows that the values of k_{8}/k_{1} for the different metal perphenyls are significantly higher than the values for i/s and somewhat less than the new values for γ_0' . If the simple mechanism given in the Introduction were to apply and if an identical donor state (S*) were involved in all three processes, the three kinetic parameters in Table I should be equal for a given metal perphenyl. These comparisons suggest first that states other than the ${}^{1}B_{2u}$ state of benzene (e.g., ion and higher excited states of the system) must be involved to an *important* extent in the high-energy sensitized decomposition. Second, if the differences between corresponding values of k_8/k_1 and γ_0' are real, there is the additional possibility of some small involvement of states other than ${}^{1}B_{2u}$ in high-energy induced luminescence. A third conclusion, stemming from the large differences between i/s and k_8/k_1 , is that the ¹B_{2u} state of benzene is involved only to a minor extent in the over-all high-energy sensitized decomposition of the metal perphenyls.

(9) Cf. W. A. Cramer, Thesis, University of Amsterdam, 1961.

⁽⁸⁾ Cf. D. F. deTar and R. A. Long, J. Am. Chem. Soc., 80, 4742 (1958); E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *ibid.*, 82, 2936 (1960); E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron*, 17, 749 (1962).