[Reprinted from the Journal of Physical Chemistry, 69, 3024 (1965).]

A Study of the Radiolysis and Luminescence Behavior of Dioxane–Benzene Mixtures

by Enrique A. Rojo[1a] and Robert R. Hentz

Department of Chemistry and Radiation Laboratory,[1b] University of Notre Dame, Notre Dame, Indiana 46556
(Received March 22, 1965)

G values for gas products in γ-irradiation of pure, liquid dioxane were constant over the dose range (0.46–4.6) $\times$ 10^{19} e.v. g.$^{-1}$. These G values for a dose rate of 1.9 $\times$ 10^{18} e.v. g.$^{-1}$ min.$^{-1}$ are as follows: H_2, 2.1; C_2H_4, 0.50; C_2H_6, 0.051; CO, 0.23; CH_4, 0.035. Study of the polymer product indicated that dioxane dimers constitute the initial polymer product. G(monomer $\rightarrow$ dimer) $\approx$ 3.9. Hydrogen, biphenyl, polymer, and relative luminescence G values (p-terphenyl as scintillator) were measured for benzene–dioxane mixtures. The parallel behavior of hydrogen and polymer G value curves suggests that a common dioxane precursor of hydrogen and polymer is protected from reaction by some kind of interaction with benzene. Kinetic analysis of the $G(H_2)$ results gives $\alpha = 0.21\ M^{-1}$ as the ratio of specific rate of excitation transfer to that of decay for the excited dioxane species that yields hydrogen. This analysis also indicates that thermal H atoms make a negligible contribution to the hydrogen yield from dioxane. A similar treatment of relative luminescence G values leads to an estimate of 65 M^{-1} as the corresponding ratio for the excited dioxane species that gives rise to luminescence. It is concluded that the latter species makes a negligible contribution to the yield of decomposition products and that the excited species that yields decomposition products is of very short lifetime. For protection to compete with decomposition it may be necessary that a molecule of benzene be a nearest neighbor to the labile excited dioxane species at the time of its formation.

Introduction

Numerous studies of decomposition, luminescence of added scintillators, and decay times in irradiated benzene, cyclohexane, and their mixtures have established significant differences in the radiation-induced behavior characteristic of these two substances.[2] Among the many interesting questions raised by these studies are the following. What relationship exists between the phenomena of and the excited states involved in protection and luminescence or the quenching of luminescence? To what characteristics of the system is the essentially different mechanism of sensitized luminescence and quenching in cyclohexane attributable as compared to that in benzene? What is the nature of the excited states involved in the various processes in the different systems—excited molecules, ions, collective excitations of the system? What is the nature of the energy deposition and localization process, and how does it depend on characteristics of the system? To contribute to our understanding of some of these problems, the radiolysis and luminescence (with added p-terphenyl) of benzene–dioxane mixtures has been investigated, and the results are reported here. Dioxane was chosen because in most respects it is similar to cyclohexane while in one very important respect it is similar to benzene: namely, in dioxane, as in benzene, the existence of a lowest electronic transition with considerable vibrational structure has been established.[3]

(1) (a) International Atomic Energy Agency, Fellow, 1963–1964, on leave from the Atomic Energy Commission of Argentina. (b) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is A.E.C. Document No. COO-38-404.

(2) Reference to all the papers devoted to these subjects would require an extensive bibliography; instead, reference is made throughout this paper to pertinent recent publications which serve as an introduction to the entire field.

(3) G. J. Hernandez and A. B. F. Duncan, *J. Chem. Phys.*, 36, 1504 (1962).

Experimental

Chemicals. The 1,4-dioxane, Fisher Certified reagent, was first purified by the method of Tunnicliff.[4] In this procedure, the dioxane is refluxed during and subsequent to addition of an aqueous $KMnO_4$–NaOH solution for a total of 30 min.; the dioxane is then salted out with NaOH and, after separation, is distilled in the presence of solid NaOH. A Nester–Faust spinning-band column was used, and the fraction boiling at 101–101.5° was collected. Dioxane purified in this manner was passed through a column of activated alumina to remove peroxides and then was recrystallized twice, rejecting one-fourth each time. No impurities were detectable by gas–liquid chromatography (a flame ionization detector was used with β,β'-oxydipropionitrile at 80° and Apiezon-L at 80–150°) or ultraviolet spectrophotometry. No peroxides were detectable with acid KI solution.

Benzene, Fisher Certified reagent, was recrystallized twice and distilled. No impurities were detectable by gas–liquid chromatography. Eastman scintillation grade *p*-terphenyl was used without further purification.

Procedures. Two-milliliter samples were degassed on a vacuum line by repeated cycles of freeze (−77°), pump, and thaw with several bulb-to-bulb distillations. The degassed samples then were sublimed into 13-mm. o.d. Pyrex ampoules fitted with break-seals, and the ampoules were sealed off. Samples were irradiated in a 10-kc. ^{60}Co source under conditions giving a dose rate of 1.87×10^{18} e.v. g.$^{-1}$ min.$^{-1}$ to a Fricke dosimeter solution using $G(Fe^{3+}) = 15.6$. Dose to a particular solution was determined by correction for the electron density of the solution relative to that of the dosimeter. All irradiations were carried out at room temperature.

Gas products were recovered by a reflux technique that has been described.[5] Fractions were collected at −77 and −196° and measured in a modified Saunders–Taylor apparatus. Gases were analyzed by mass spectrometry.

For study of the polymer product it was necessary to irradiate separate samples to considerably higher doses than were used for study of gas products. An aliquot of irradiated sample, of a size dependent on dose, was transferred to a weighed bulb which was attached to the vacuum line. Benzene, dioxane, and volatile products were slowly sublimed from the solidified sample into a bulb at −196° until a residue remained that appeared to be free of volatile material. This process ordinarily required 1–2 hr. Transfer then was allowed to proceed for several more minutes. For determination of polymer yield the residue was weighed and dissolved in a measured volume of hexane. This solution was analyzed by gas–liquid chromatography (Apiezon-L at 80–150° and silicone grease at 80–200°), and the weight of polymer was obtained by correction of the weight of residue for the amounts of benzene and dioxane found. The sublimate also was analyzed chromatographically for peaks characteristic of the polymer. Only those peaks characteristic of the most volatile polymer components were present in measurable amount and corresponded to less than 2 or 3% of the corresponding peaks in the polymer fraction. Thus, a negligible fraction of total polymer was present in the sublimate, and no correction was made. Reproducibility of polymer determinations was about 5%. Special care was taken to minimize exposure to air although no increase in weight of polymer was observed after standing in air for about 24 hr. The molecular weight of polymer was determined by the Rast method using a known weight of polymer obtained from another aliquot of irradiated sample by the method described. Biphenyl yields were determined in separate irradiations by chromatographic analysis of the liquid.

An apparatus and procedure described in a previous publication[6] was used to measure relative luminescence intensities from 25 ml. of degassed, γ-irradiated solutions of benzene and dioxane containing 2.17×10^{-3} *M* *p*-terphenyl.

Results

G values (100-e.v. yields) for gas products in irradiation of pure, liquid dioxane were constant over the dose range $(0.46–4.6) \times 10^{19}$ e.v. g.$^{-1}$. Thus zero-dose *G* values are indicated. These *G* values are as follows (with *G* values of Llabador and Adloff,[7] for doses in excess of 10^{21} e.v. g.$^{-1}$, in parentheses): H_2, 2.1 (2.1); C_2H_4, 0.50 (0.56); C_2H_6, 0.051 (0.055); CO, 0.23 (0.30); CH_4, 0.035 (0.046). At the high doses used by Llabador and Adloff, it was found necessary to protect initially formed C_2H_4 and CO from subsequent decomposition by addition of I_2 in order to obtain the dose-independent *G* values given in parentheses for these compounds. The addition of I_2 was found by these authors to suppress $G(CH_4)$ and $G(C_2H_6)$ by 60 and 40%, respectively, with no effect on $G(H_2)$. The results of these authors also indicate an induction period for CH_4 and C_2H_6 formation which suggests that these are secondary products. Our results, to the contrary, show no induction period and give *G* values for CH_4 and C_2H_6 comparable to those of Llabador and Adloff although the latter were

(4) D. D. Tunnicliff, *Talanta*, **2**, 341 (1959).

(5) W. Van Dusen, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 3648 (1962).

(6) M. Burton, P. J. Berry, and S. Lipsky, *J. chim. phys.*, **52**, 657 (1955).

(7) Y. Llabador and J. P. Adloff, *ibid.*, **61**, 681 (1964).

calculated for a dose three orders of magnitude greater than the dose used in our work. Ethanol and acetaldehyde were identified among the liquid products, but quantitative determinations were not made.

The polymer product from pure dioxane is a pale yellow, viscous liquid. Both the color and viscosity increase with increase in dose. Chromatographic analysis of the polymer formed at 1.21×10^{21} e.v. g.$^{-1}$ showed at least 15 peaks. Comparison of the total peak area to the weight of polymer suggests that an appreciable fraction of the polymer of high molecular weight escaped detection. In samples irradiated at low doses, small white crystals become visible in the polymer after standing several hours. On gentle heating, even at atmospheric pressure, the white crystals can be sublimed out of the polymer and collected in an adjacent trap. The crystals do not reappear in the polymer. The isolated white crystals dissolved in hexane give two peaks in chromatography that correspond to the two principal peaks obtained in chromatographic analysis of the entire polymer product at low dose. These two products were separated by crystallization from methanol. Melting points of 130 and 156° and a molecular weight of 168, for both products, were obtained. These values are consistent with identification of the products as the *meso* and racemic forms of dioxanyldioxane.[8]

G(polymer)[9] and molecular weight of polymer are given in Figure 1 as a function of dose in pure, liquid dioxane. Rough extrapolations to zero dose give G(polymer) $\approx$ 3.9 and molecular weight $\approx$ 174. The zero-dose molecular weight indicates that dioxane dimers are the initial polymer products and higher molecular weight polymers are secondary products. Llabador and Adloff[7] obtained G(polymer) = 3.65. In pure, liquid benzene, G(polymer) = 0.97 was obtained at a dose of 1.20×10^{21} e.v. g.$^{-1}$. This value is in good agreement with other reported values for ^{60}Co radiation.[10]

Hydrogen, biphenyl, polymer, and relative luminescence yields are given for benzene–dioxane solutions in Figures 2 and 3.

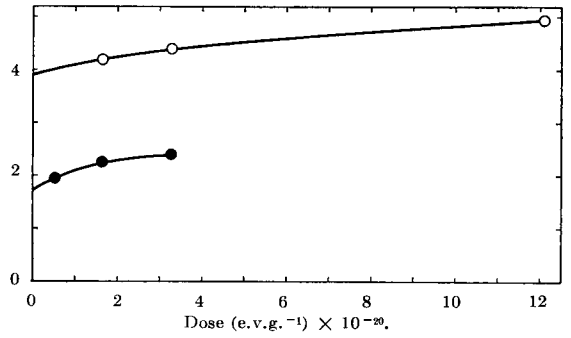

Figure 1. Molecular weight and G value of polymer as a function of dose in γ-irradiation of dioxane: ○, G(polymer); ●, molecular weight × 10^{-2}.

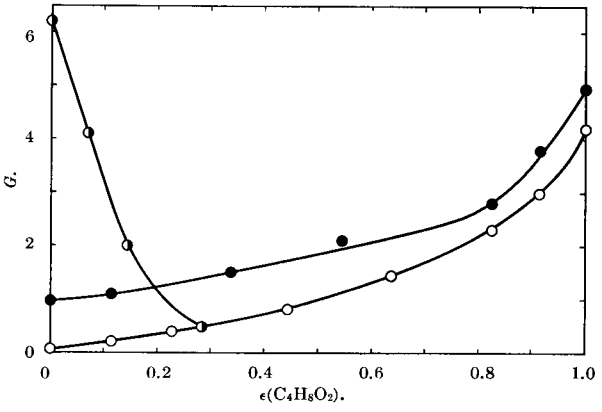

Figure 2. Yields of hydrogen, biphenyl, and polymer in γ-irradiation of benzene–dioxane mixtures: ○, $G(H_2) \times 2$, dose = 9.2×10^{18} e.v. g.$^{-1}$; ◑, $G(C_{12}H_{10}) \times 10^2$, dose = 1.09×10^{20} e.v. g.$^{-1}$; ●, G(polymer), dose = 1.20×10^{21} e.v. g.$^{-1}$.

Discussion

Effects in Pure Dioxane. The zero-dose polymer appears to be essentially pure dimer. Consequently, the relationship

$$G(H_2) - (1/2)G_0(\text{polymer}) = 2.1 - 3.9/2 = 0.15 \quad (1)$$

suggests that the major *over-all* reaction in radiolysis of pure liquid dioxane is

$$C_4H_8O_2 \longrightarrow {}^1/_2(C_4H_7O_2)_2 + {}^1/_2H_2 \quad (I)$$

with $G \approx 3.9$. Because 3.9 is an imprecise, extrapolated value, no precise significance can be attached to the 0.15 excess of $G(H_2)$ in eq. 1. However, small yields of hydrogen-deficient products (*e.g.*, G(CO) = 0.23) do require hydrogen in stoichiometric excess over polymer. In radiolysis of dioxane, in contrast to cyclohexane,[11] ring fragmentation plays a significant role even in the liquid state; notably, $G(C_2H_4)$ = 0.50 in dioxane as

(8) K. Pfordte, *Ann. Chem.*, 625, 30 (1959).

(9) G(polymer) is calculated on the basis of monomer units in the polymer. In the mixtures the extent to which each monomer is incorporated in the polymer is uncertain. For calculation of G(polymer) in the mixtures, the average molecular weight of the mixture was used. Since the molecular weights of benzene and dioxane differ by only 12%, little uncertainty is caused by this procedure.

(10) S. Gordon, A. R. Van Dyken, and T. F. Doumani, *J. Phys. Chem.*, 62, 20 (1958); W. G. Burns and C. R. V. Reed, *Trans. Faraday Soc.*, 59, 101 (1963); T. Gaumann, *Helv. Chim. Acta*, 44, 1337 (1961); T. Gaumann, *ibid.*, 46, 2873 (1963); J. Lamborn and A. J. Swallow, *J. Phys. Chem.*, 65, 920 (1961).

(11) S. K. Ho and G. R. Freeman, *ibid.*, 68, 2189 (1964).

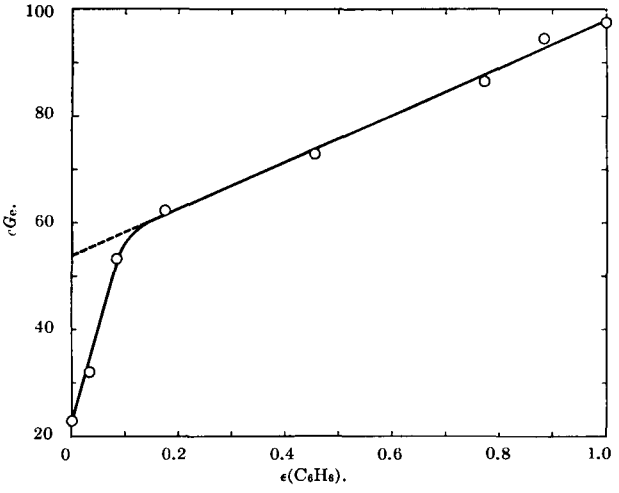

Figure 3. Relative luminescence yields in γ-irradiation of air-free mixtures of benzene and dioxane with 2.17×10^{-3} M p-terphenyl.

compared to $G(C_2H_4) = 0.12$ in cyclohexane.[12] Mass 28 is the major peak in the 70-v. mass spectrum of dioxane, exceeding in magnitude that of the parent ion by a factor of about 3.3.[13] Minor fragmentation processes (*e.g.*, that which gives a mass-15 peak 17% of the mass-28 peak in the 70-v. mass spectrum) can account for formation of small yields of methane and ethane as initial, rather than as secondary, products. The observed increases in molecular weight and yield of polymer with increase in dose suggest the addition of radicals, which otherwise would dimerize or disproportionate, to initially formed unsaturated products which are converted thereby into polymer of higher molecular weight than the dimer.

Benzene–Dioxane Mixtures; Hydrogen Yields. The hydrogen yield curve of Figure 2 suggests a protective effect of benzene[14] on dioxane. Such an effect is consistent with lower values of ionization potential and energy of the first electronic transition for benzene[15] as compared to dioxane.[3] It is instructive to treat the hydrogen yields in the manner of Merklin and Lipsky.[16] In the reaction sequence and associated table of rates

$$\begin{aligned}
\mathrm{D} &\xrightarrow{\sim} \mathrm{D}^* && \epsilon_D R_0 G_D^*/N_0 \\
\mathrm{B} &\xrightarrow{\sim} \mathrm{B}^* && \epsilon_B R_0 G_B^*/N_0 \\
\mathrm{D}^* &\longrightarrow \mathrm{H_2} && k_1[\mathrm{D}^*] \\
\mathrm{D}^* &\longrightarrow \text{no } \mathrm{H_2} && k_2[\mathrm{D}^*] \\
\mathrm{B}^* &\longrightarrow \mathrm{H_2} && k_3[\mathrm{B}^*] \\
\mathrm{B}^* &\longrightarrow \text{no } \mathrm{H_2} && k_4[\mathrm{B}^*] \\
\mathrm{D}^* + \mathrm{B} &\longrightarrow \mathrm{D} + \mathrm{B}^* && k_5[\mathrm{D}^*][\mathrm{B}]
\end{aligned}$$

D and B refer respectively to dioxane and benzene, ϵ_D and ϵ_B to their electron fractions, R_0 to the dose rate in units of 100 e.v. l.$^{-1}$ sec.$^{-1}$, and G_D^* and G_B^* to 100-e.v. yields of D* and B*. The steady-state treatment, based on the assumption that absorbed energy is partitioned in proportion to electron fraction, yields a Merklin–Lipsky equation

$$\eta \equiv \frac{\epsilon_D(G_D - G_B)}{(G - G_B)} = \frac{1 + \alpha[\mathrm{B}]}{1 + \gamma[\mathrm{B}]} \qquad (2)$$

where G, G_D, and G_B refer to 100-e.v. hydrogen yields from the mixture, pure dioxane, and pure benzene, respectively; $\alpha = k_5/(k_1 + k_2)$ and $\gamma = \alpha G_B(G_D^*/G_B^* - 1)/(G_D - G_B)$.

A plot of η as a function of [B][17] is shown in Figure 4 with the least-square line based on all points except that for the highest benzene concentration (90 mole %). Thus, γ[B] would appear to be $\ll 1$ over the whole

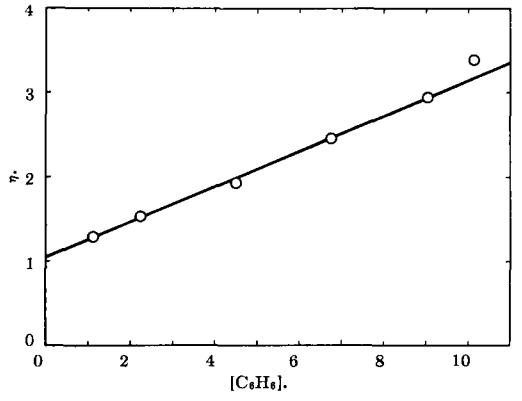

Figure 4. Dependence of η on molarity of benzene in γ-irradiation of benzene–dioxane mixtures; dose = 9.2×10^{18} e.v. g.$^{-1}$.

(12) S. Sato, K. Kikuchi, and S. Shida, *J. Chem. Phys.*, **41**, 2216 (1964).

(13) American Petroleum Institute Research Project 44, National Bureau of Standards, Catalog of Mass Spectral Data, Serial No. 450, contributed by the Humble Oil and Refining Co., Baytown, Texas.

(14) *Cf.* J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952); M. Burton, S. Gordon, and R. R. Hentz, *J. chim. phys.*, **48**, 190 (1951).

(15) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(16) J. F. Merklin and S. Lipsky, *J. Phys. Chem.*, **68**, 3297 (1964).

(17) No special significance with respect to mechanism is implied in use of molarity as the benzene concentration unit. This unit is employed by Merklin and Lipsky; it also permits a direct comparison with the luminescence behavior of this system. In view of the high benzene concentrations required for significant protection, it is clear that the rate of the excitation-transfer process involved cannot be determined by simple second-order kinetics. On the contrary, it is possible that this rate is related to the probability that a benzene molecule is a nearest neighbor to an excited dioxane molecule at the time of its formation. In this case, mole fraction would be the appropriate concentration unit. Since the ratio of molarity to mole fraction varies by less than 4% over the concentration range used in this work, the analysis is not affected significantly by the choice of concentration unit.

range of [B]. From the slope of the least-square line a value of $\alpha = 0.21\ M^{-1}$ is obtained. In accordance with the interpretations of Merklin and Lipsky, the intercept, $\eta = 1.04$, indicates that essentially all of the hydrogen yield from dioxane conforms to the postulated mechanism and can be suppressed by energy transfer to benzene. The results are thus consistent with the assumption of the mechanism that thermal H atoms (if produced) make negligible contribution to the hydrogen yield from dioxane. Such a conclusion is consistent with the observation of a negligible effect of added iodine on $G(H_2)$ from dioxane.[7] In this view, formation of hydrogen in γ-irradiation of pure, liquid dioxane must occur *via* the elimination of molecular hydrogen or the formation of "hot" H atoms or both. However, the major hydrogen formation processes should conform to the stoichiometry of reaction I, consistent with the near equality of hydrogen and dimer yields shown in eq. 1. Elimination of molecular hydrogen from a single molecule would not conform to the necessary stoichiometry unless both H atoms come from the same carbon atom which then inserts into a C–H bond of another dioxane molecule; nor would any reaction giving rise to dioxanyl radicals conform to the necessary stoichiometry, *e.g.*, formation of "hot" H atoms, unless the ratio of disproportionation to combination is negligible. Dioxene was not sought in this work; however, it was not reported by Llabador and Adloff,[7] who determined the liquid products.

Polymer and Biphenyl Yields in Mixtures. If the assumption is valid that absorbed energy is partitioned in proportion to electron fraction, then the polymer yield curve of Figure 2 constitutes rather conclusive evidence, in support of the analysis of hydrogen yield data, that dioxane is protected by energy transfer to benzene. At the very least, in the absence of any interaction, the polymer yield curve should be a straight line joining the extreme values of G(polymer) for the pure components. However, benzene appears to react rapidly with free radicals such as phenyl[18] and cyclohexyl.[19] Thus, if dioxanyl radicals are intermediates in formation of dioxane dimer, then addition of these radicals to benzene molecules, with increasing concentration of the latter, would result in conversion of more solvent monomer units to polymer than if the dioxanyl radicals simply recombined as in pure dioxane; under these circumstances, the polymer yield curve would lie above the straight line expected for no interaction. Because of the large doses necessitated in the polymer study and because of a lack of precise knowledge concerning all the elementary reactions involved in polymer formation in the mixtures, kinetic analysis of the polymer yield curve is not warranted. Very definitely, the parallel behavior of the curves in Figure 2 for G(polymer) and $G(H_2)$ suggests that a common dioxane precursor of polymer and hydrogen is protected from reaction by some kind of interaction with benzene.

Work in this laboratory by Cramer[20] has shown that the mechanism of biphenyl formation in radiolysis of benzene appears to involve addition of phenyl radicals to benzene followed by disproportionation and combination reactions of the radical $C_6H_5C_6H_6$.[18] With addition of dioxane, particularly because G(radical) is probably larger for dioxane than for benzene, the probability of disproportionation of $C_6H_5C_6H_6$ to biphenyl will change as a result of change in the nature of the radicals most frequently encountered by $C_6H_5C_6H_6$. Further, the reaction

$$C_6H_5 + C_4H_8O_2 \longrightarrow C_6H_6 + C_4H_7O_2 \qquad \text{(II)}$$

may compete with addition of C_6H_5 to benzene. Again, in the absence of precise knowledge concerning all the elementary reactions involved, a kinetic analysis of the biphenyl yield data is not warranted. However, the rather sharp suppression of biphenyl yields on addition of dioxane to benzene (*cf.* Figure 2) seems more consistent with an appreciable role of reaction II than with a large change in the probability of disproportionation of $C_6H_5C_6H_6$ to biphenyl.

Relative Luminescence Yields. The relative luminescence yields may be analyzed in terms of a set of reactions and by a method analogous to those used in analysis of the hydrogen yields, but with some very significant differences.

$$\mathrm{D} \xrightarrow{\sim} \mathrm{D}^{\pm} \quad \epsilon_D R_0 G_D{}^{\pm}/N_0$$

$$\mathrm{B} \xrightarrow{\sim} \mathrm{B}^{\pm} \quad \epsilon_B R_0 G_B{}^{\pm}/N_0$$

$$\mathrm{D}^{\pm} \longrightarrow \mathrm{D} \text{ or product} \quad k_D[D^{\pm}]$$

$$\mathrm{D}^{\pm} + \mathrm{X} \longrightarrow \mathrm{D} + \mathrm{X}^* \quad k_{DX}[\mathrm{D}^{\pm}][\mathrm{X}]$$

$$\mathrm{D}^{\pm} + \mathrm{B} \longrightarrow \mathrm{D} + \mathrm{B}^{\pm} \quad k_{DB}[\mathrm{D}^{\pm}][\mathrm{B}]$$

$$\mathrm{B}^{\pm} \longrightarrow \mathrm{B} \text{ or product} \quad k_B[\mathrm{B}^{\pm}]$$

$$\mathrm{B}^{\pm} + \mathrm{X} \longrightarrow \mathrm{B} + \mathrm{X}^* \quad k_{BX}[\mathrm{B}^{\pm}][\mathrm{X}]$$

$$\mathrm{X}^* \longrightarrow \mathrm{X} \quad k_X[\mathrm{X}^*]$$

$$\mathrm{X}^* \longrightarrow \mathrm{X} + h\nu \quad k_e[\mathrm{X}^*]$$

All previously used symbols have the same signifi-

(18) C. A. Barson and J. C. Bevington, *Trans. Faraday Soc.*, 55, 1266 (1959); E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, 82, 2936 (1960).

(19) T. Gaumann, *Helv. Chim. Acta*, 44, 1337 (1961).

(20) W. A. Cramer, Thesis, University of Amsterdam, 1961. *Cf.* E. A. Cherniak, E. Collinson, and F. S. Dainton, *Trans Faraday Soc.*, 60, 1408 (1964).

cance, except that the possibility of different excited states, $D^{\pm}$ and $B^{\pm}$, being involved is specifically noted by a change in superscript. In addition, X denotes *p*-terphenyl and k_D, k_B, and k_X are summed rate constants for all reactions of $D^{\pm}$, $B^{\pm}$, and X^*, respectively, other than the excitation-transfer and emission processes specifically written for these species. The steady-state treatment gives

$$\frac{\epsilon_D(\rho_D G_D{}^{\pm} - \rho_B G_B{}^{\pm})}{G_e/f - \rho_B G_B{}^{\pm}} = \frac{1 + \alpha'[B]}{1 + \gamma'[B]} \quad (3)$$

where

$$\rho_D = k_{DX}[X]/(k_D + k_{DX}[X]) \quad (4)$$

$$\rho_B = k_{BX}[X]/(k_B + k_{BX}[X]) \quad (5)$$

$$\alpha' = k_{DB}/(k_D + k_{DX}[X]) = \rho_D k_{DB}/k_{DX}[X] \quad (6)$$

$$\gamma' = \alpha'\rho_B G_B{}^{\pm}(G_D{}^{\pm}/G_B{}^{\pm} - 1)/(\rho_D G_D{}^{\pm} - \rho_B G_B{}^{\pm}) \quad (7)$$

$$f = k_e/(k_e + k_X) \quad (8)$$

and G_e is the 100-e.v. yield of luminescence photons.

The results of Burton, *et al.*,[21] suggest that for *p*-terphenyl in degassed dioxane, a reasonable value of $Q_D' \equiv k_D/k_{DX}$ would be about $4 \times 10^{-3}\ M$ ($Q' = 2.8 \times 10^{-3}\ M$ was reported for cyclohexane). If the assumption is made that $k_{DX} = 3k_{DB}$, then $k_D/k_{DB} = 12 \times 10^{-3}\ M$ and about 90% of $D^{\pm}$ transfer their excitation to benzene at $[B] = 0.1\ M$, which corresponds to about 1 vol. % of benzene. However, in a variety of systems ("common" solvent + benzene + scintillator) Q and Q' values show a significant change as benzene concentration increases above 1 vol. % and do not become characteristic of pure benzene until a concentration near 20 vol. % is reached.[21]

In Figure 3, the relative luminescence yield, cG_e (relative luminescence intensity divided by dose rate), is plotted against ϵ_B. It is evident that some process approaches completion near 20 vol. % of benzene.[22] If $\alpha'[B]$ is large compared to both unity and $(\rho_D G_D{}^{\pm} - \rho_B G_B{}^{\pm})/(\rho_B G_D{}^{\pm} - \rho_B G_B{}^{\pm})$, then 1 can be dropped in both numerator and denominator on the right-hand side of eq. 3, and eq. 3 can be transformed into eq. 9 where c is

$$cG_e = cf[\rho_B G_D{}^{\pm} + (G_B{}^{\pm} - G_D{}^{\pm})\rho_B\epsilon_B] \quad (9)$$

a constant which relates G_e to the measured relative luminescence yield. For values of $\epsilon_B \geqq 0.175$ the plot of cG_e against ϵ_B in Figure 3 conforms very well to the least-square line

$$cG_e = 53.9 + 44.0\epsilon_B \quad (10)$$

From the values obtained for $cG_e = cf\rho_B G_D{}^{\pm}$ and $cf\rho_B G_B{}^{\pm}$ at $\epsilon_B = 0$ and 1, respectively, in eq. 10 and from the experimental value of $cG_e = cf\rho_D G_D{}^{\pm}$ at $\epsilon_B = 0$, the following ratios are obtained.

$$G_D{}^{\pm}/G_B{}^{\pm} = 0.55 \quad (11)$$

$$\rho_B/\rho_D = 2.3 \quad (12)$$

For *p*-terphenyl in pure, degassed benzene, Burton, *et al.*,[21] report $Q_B' = 10^{-3}\ M$. Use of this value and eq. 12 gives $Q_D' = 5.1 \times 10^{-3}\ M$. Thus, $\alpha' = 46\ M^{-1}$ (assuming $k_{DX} = 3k_{DB}$) and at $\epsilon_B = 0.175$, $\alpha'[B] = 104$ which is indeed large compared to both unity and to the value of $(\rho_D G_D{}^{\pm} - \rho_B G_B{}^{\pm})/(\rho_B G_D{}^{\pm} - \rho_B G_B{}^{\pm}) = 1.7$.

Some Conclusions and Speculation. From the value of $\alpha' = 46\ M^{-1}$, a value of $\alpha^{\pm}$ (for $D^{\pm}$ which results in luminescence) $= \alpha'(1 + [X]/Q_D') = 65\ M^{-1}$ is obtained. This result may be compared with $\alpha = 0.21\ M^{-1}$ for D^* which gives rise to hydrogen. It is evident that $D^{\pm}$ and D^* are different and, therefore, that $D^{\pm}$ makes a negligible contribution to the yield of chemical decomposition. Either $G_D{}^{\pm}$ is small compared to $G(H_2) = 2.1$, equivalent to $k_1 G_D{}^*/(k_1 + k_2)$, or a small fraction of the molecules $D^{\pm}$ decomposes.

Since the first electronic transition in dioxane shows considerable vibrational structure,[3] the corresponding excited state should have a lifetime of the order of 10^{-8} sec. Consequently, it is tempting to identify $D^{\pm}$ with this lowest electronic transition, as has been done in the case of benzene.[23] However, a positive identification must await measurement of the decay time of $D^{\pm}$ and measurement of Q_D' for ultraviolet excitation. It is of interest to note that the value of $Q_D' = 5.1 \times 10^{-3}\ M$, in contrast with the Q' values for benzene and cyclohexane,[21] is compatible with a diffusion-controlled, energy-transfer reaction for reasonable values of all parameters (sum of diffusion coefficients $\approx 4 \times 10^{-5}$ cm.^{2}/sec., sum of the van der Waals radii ≈ 5 Å., decay time of $D^{\pm} \approx 1.2 \times 10^{-8}$ sec.).[24] One might say that the behavior of dioxane is "normal" in that it may not be necessary to invoke any special attributes to interpret luminescence and quenching parameters, contrary to the situation in benzene and cyclohexane.[21,23,24]

The value of $\alpha = 0.21\ M^{-1}$ suggests that the states represented by D^*, which yield decomposition products, have a very short lifetime. Thus, the fraction of D^*

(21) M. Burton, M. A. Dillon, C. R. Mullin, and R. Rein, *J. Chem. Phys.*, 41, 2236 (1964).

(22) The value of $\epsilon_B = 0.175$ corresponds to 20 vol. % and 2.25 *M*.

(23) S. Lipsky and M. Burton, *J. Chem. Phys.*, 31, 1221 (1959); J. L. Kropp and M. Burton, *ibid.*, 37, 1742 (1962).

(24) C. R. Mullin, M. A. Dillon, and M. Burton, *ibid.*, 40, 3053 (1964).

protected from decomposition in essentially pure benzene, 11.27 M, is only 0.71. For protection to compete with decomposition it may be necessary that a molecule of protective agent be a nearest neighbor to an excited or ionized molecule at the time of its formation. Protection by charge or excitation transfer may be in competition with such processes of short lifetime as decomposition of an ion before neutralization, geminate recombination of an ion and its electron, or decomposition of highly excited molecules formed either directly or on ion neutralization. Whatever the process being prevented, it is responsible for essentially the total yield of chemical decomposition. These conclusions would also appear to apply to benzene[25] and to cyclohexane (compare $\alpha = 0.84\ M^{-1}$ for benzene in cyclohexane[16] and $1/Q' = 360$ for p-terphenyl in cyclohexane[21]).

Acknowledgment. The authors are grateful to Dr. M. Burton for suggestion of this problem and for helpful advice.

(25) H. F. Barzynski, R. R. Hentz, and M. Burton, to be published; D. B. Peterson, T. Arakawa, D. A. G. Walmsley, and M. Burton, to be published.