intensity in glacial acetic acid solutions. It is not known how much of this effect is due to change in dielectric constant with change of solvents.

Weaks resonances are also observed for the reactive butyrophenones at about $g = 4$. n,π^* triplets have not been observed previously by epr techniques. This has been attributed to large zero-field splittings resulting from magnetic dipole interactions between the electrons in the "localized" n,π^* state. Thus the n,π^* epr spectrum is expected to lie outside the frequency limits that are ordinarily observed. Also, the short lifetimes and attendant low steady-state concentrations of n,π^* triplets preclude convenient observation of these resonances. We are continuing our investigation into this matter.

We are also studying structural effects at the γ position of the alkyl chain. Thus γ-phenylbutyrophenone has a large ϕ_{II}, 0.49. It is interesting that the major peak in the mass spectrum of this compound is at m/e 120 and arises from the electron-impact-induced rearrangement analogous to the photochemical "type II" split.[32] These results seem to reflect the different lability of primary and secondary hydrogen atoms on carbon chains as well as the presence of the γ-phenyl group. Walling and Gibian also found that the triplet state of benzophenone is extremely sensitive to C–H bond strength.[14] They further find that benzophenone is unreactive toward acetic acid. This indicates, as implied above, that the triplet's reactivity is based on its ability to attract the σ electron enveloping the hydrogen atom.

Acknowledgment. This work was supported by Grant AP 00109 of the Division of Air Pollution, Bureau of State Services, Public Health Service. E. J. B. also wishes to acknowledge a Public Health Special Fellowship 5 F3 AP-16, 569-03, from the Division of Air Pollution.

(32) For a discussion of possible correlations between photoelectron- and γ-ray-initiated intramolecular processes and earlier references, see J. N. Pitts, Jr., J. K. Foote, and J. K. S. Wan, *Photochem. Photobiol.*, **4**, 323 (1964); see also D. J. Coyle, *J. Phys. Chem.*, **67**, 1800 (1963).

Triplet States in Radiation Chemistry. Radiochemical *cis–trans* Isomerization

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Abstract: Radiation-induced *cis–trans* isomerization of three pairs of olefins has been studied by determination of both initial rates of isomerization and the composition of radiostationary states. The data correlate strikingly well with data obtained in sensitized photoisomerization reactions of the same substrates. Consequently, we infer that isomerization involves formation and decay of excited triplet states of the olefins. The sum of the *G* values for the *trans* → *cis* and *cis* → *trans* reactions is taken as the value of *G* for formation of olefin triplets. Except in very concentrated solutions most of the excitation must be first absorbed by the solvent and then transferred to the solute. The highest yield of triplets measured in benzene was 9.9, and a value of 20 was estimated in an experiment in which pure *cis*-stilbene was irradiated. The very high *G* values for triplets are attributed to the fact that reactive energy acceptors can compete effectively with triplet–triplet annihilation reactions in regions of high excitation density within spurs.

Benzene and aromatic compounds in general are relatively stable toward degradation by ionizing radiation. This stability may be attributed to the availability of electronic excited states having little probability of dissociation. It has been suggested[3–5] that at least part of the yield of biphenyl, partially reduced biphenyls, and hydrogen in the radiolysis of benzene may arise from bimolecular reactions of electronically excited states within spurs. Recently, correlations have been made between triplet-state photochemical reactions and radiolyses.[6] Our interest was aroused by the question of the nature, role, and yield of excited states in radiation chemistry. We were particularly interested in comparing chemical phenomena observed with radiation-produced excited states to those observed in photochemistry.

No data are available that give a convincing value for the total yield of any excited state of benzene though several attempts have been made. Cherniak, Collinson, and Dainton[3] have estimated *G* (100-ev yield) for excited benzene to be 1.35 from $FeCl_3$ radical-scavenging experiments in which an excited state was invoked to explain the shape of the $G(-FeCl_3)$ *vs.* $FeCl_3$ concentration curve. Recent work of Nosworthy[7] and of Fischer, Lehman, and Stein[8] on the *cis–trans* isomerization of the maleate–fumarate and stilbene pairs, respectively, gives a value of 1.0–1.1 for the yield of benzene triplets. The extensive work of Cundall and Griffiths[9] has led to

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(1) National Science Foundation Postdoctoral Fellow, 1964–1965.

(2) National Institutes of Health Postdoctoral Fellow, 1965–1966.

(3) E. A. Cherniak, E. Collinson, and S. S. Dainton, *Trans. Faraday Soc.*, **60**, 1408 (1964).

(4) J. Y. Yang, J. D. Strong, and J. G. Burr, *J. Phys. Chem.*, **69**, 1157 (1965).

(5) W. G. Burns, *Trans. Faraday Soc.*, **58**, 961 (1962).

(6) See, for example, P. Dunion and C. N. Trumbore, *J. Am. Chem. Soc.*, **87**, 4211 (1965), and references therein.

(7) J. Nosworthy, *Trans. Faraday Soc.*, **61**, 1138 (1965).

(8) E. Fischer, H. P. Lehman, and G. Stein, *Chem. Commun.* 583 (1965). We thank Professor Stein for a preprint of this work.

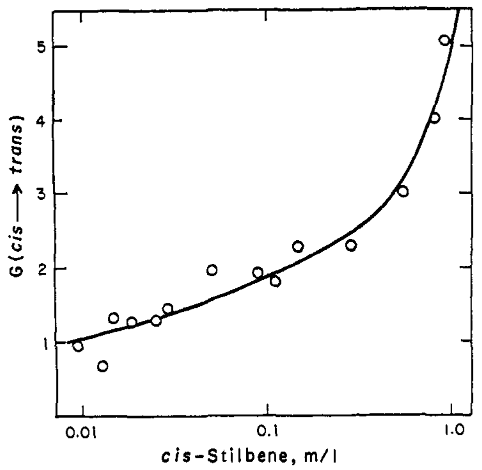

Figure 1. Radiation-induced isomerization of *cis*-stilbene in degassed benzene solution.

an estimate of G(triplet benzene) = 4.23 based on the apparent limiting value of *cis–trans* isomerization in benzene solutions of the 2-butenes.

Our own work involves the radiochemical changes in benzene solutions containing solutes (the stilbenes, 1,2-diphenylpropenes, 2,3-diphenyl-2-butenes, and piperylenes) which have been studied carefully as substrates in sensitized photoreactions.[10] Our results suggest that the yield of triplet states, taking together solvent and solute triplets, must be considerably higher than has been estimated by any other method. These results, together with evidence obtained from studies of the scintillation process, indicate that most of the excitation energy delivered to a material having relatively stable excited states decays by way of the lowest triplet state of the system.

Results and Discussion

Radiochemical *cis–trans* Isomerizations. As in the case of photosensitized isomerizations, two types of measurements have been used to characterize the systems. The *cis–trans* isomerization reaction were carried out to low conversion (5–20%), and the G values obtained were then converted to initial G values (100-ev yield extrapolated to 0% conversion) by correcting for back reaction.[11] We define the following symbols: G_T = initial yield of substrate triplets, $G_{c,t}$ = initial yield of *trans* from pure *cis*, and $G_{t,c}$ = initial yield of *cis* from pure *trans*. Mixtures were also irradiated for long times to determine their composition after establishment of radiostationary states.

Radiostationary states were established for the stilbenes, 1,2-diphenylpropenes, and piperylenes (1,3-pentadienes) by irradiating dilute (*ca.* 0.03 *M*) solutions of both isomers for long periods. As is shown by the data in Table I, there is excellent agreement between measured radiostationary states and photostationary states established with high-energy sensitizers such as acetophenone and benzophenone. The triplet energy of benzene is sufficiently high (84 kcal/mole) so that each of the substrates examined would be expected to quench benzene triplets at the diffusion-controlled rate. In the case of the 1,2-diphenylpropenes, long-term irradiation of dilute benzene solutions led only to isomerization. The recovery after 120 hr of irradiation (5×10^{21} ev dose) was about 90%. With the stilbenes, formation of phenanthrene was observed in addition to isomerization. Slow decomposition, in addition to phenanthrene formation, was observed with the stilbenes, but no additional products were detected. Disappearance of piperylene was also noted; the behavior of piperylene on γ irradiation in benzene solutions is very similar to that observed in irradiation of the same solutions with 2537-A light.[12] Apparently, decomposition of stilbene and piperylene is slow compared with establishment of a stationary state since the composition of the stationary state is independent of the extent of decomposition.

Table I

Starting material	Radiostationary state, benzene, %	"High-energy" photostationary state,[a] %
cis- and *trans*-stilbene	58.79, *cis*	59.4, *cis*
cis- and *trans*-1,2-diphenylpropene	54.65, *cis*	54.75, *cis*
trans-Piperylene	57.5, *trans*	56.5, *trans*

[a] Average value for "high-energy" photostationary state.

$G_{c,t}$ values are plotted against the logarithm of the *cis*-stilbene concentration in Figure 1. Similar plots, displaced along the ordinate, are obtained when plots are made for isomerization of *trans*-2,3-diphenyl-2-butene and *cis*- and *trans*-1,2-diphenylpropene. At any concentration, the ratio of $G_{c,t}$ to $G_{t,c}$ is 0.72 ± 0.05 for the stilbenes and 0.84 ± 0.05 for the 1,2-diphenylpropenes. The ratio $G_{t,c}/(G_{t,c}\ c + G_c,\ t)$ is 0.58 ± 0.04 for stilbenes and 0.54 ± 0.01 for the 1,2-diphenylpropenes. The yield ratios are the same in each case as those measured when irradiation with light, absorbed by high-energy sensitizers in dilute solutions, is continued until a *cis–trans* stationary state is obtained.

We propose the following mechanism, essentially identical with that of Cundall,[9] to explain our results. The crucial features of the mechanism are that k_2

$$C_6H_6 \rightsquigarrow \longrightarrow (C_6H_6)^3 \qquad (1)$$

$$(C_6H_6)^3 + cis\text{-olefin} \xrightarrow{k_2} C_6H_6 + (\text{olefin})^3 \qquad (2)$$

$$(C_6H_5)^3 + trans\text{-olefin} \xrightarrow{k_3} C_6H_6 + (\text{olefin})^3 \qquad (3)$$

$$(C_6H_6)^3 \longrightarrow C_6H_6 \qquad (4)$$

$$(\text{olefin})^3 \xrightarrow{k_5} cis\text{-olefin} \qquad (5)$$

$$(\text{olefin})^3 \xrightarrow{k_6} trans\text{-olefin} \qquad (6)$$

= k_3 = k (diffusion) and that the photochemically determined ratio of k_6 to k_5 gives the ratio of G's. On this basis $G_{t,c} + G_{c,t}$ is the yield of scavenger molecules that become excited and ultimately decay by way of their triplet states.

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(9) (a) R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965); (b) R. B. Cundall and P. A. Griffiths, *J. Phys. Chem.*, **69**, 1866 (1965); (c) R. B. Cundall and P. A. Griffiths, *Discussions Faraday Soc.*, **36**, 111 (1963); (d) R. B. Cundall and P. A. Griffiths, *J. Am. Chem. Soc.*, **85**, 1211 (1963).

(10) See, for example, G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964), and other papers in this series.

(11) The method of A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965), was used for this correction.

(12) L. M. Stephenson, unpublished results.

There is one set of data that are not in agreement with this interpretation. In a similar study, Burton, Hentz, and their co-workers have found that the *G* values for radiation-induced isomerization of *trans*-stilbene do not increase in the same way as those for isomerization of the *cis* isomer when the concentration is increased above 0.1 *M*.[13] Although we have not carried studies with *trans*-stilbene to concentrations as high as those studied by the Notre Dame group, preliminary studies with concentrations up to 0.4 *M* convince us that their observation is correct. In our work we devoted most attention to the 1,2-diphenylpropenes because the system is chemically cleaner. As is shown by the data in Table II, the ratio of *G* values remains constant up to 1 *M* concentration. At that concentration, $G_{t,c} + G_{c,t}$ is 9.9. Obviously both of the diphenylpropenes behave in the same way as *cis*-stilbene.

Table II. Radiolytic *cis–trans* Isomerization of 1,2-Diphenylpropene in Benzene

Isomer	Electron fraction	Concn, *M*	$G_{c,t}$	$G_{t,c}$	G_T
cis		1.045	4.45		
	0.22				9.93
trans		1.056		5.48	
cis		0.546	3.47		
	0.11				7.40
trans		0.525		3.93	
cis		0.151	2.32		
	0.03				5.32
trans		0.152		3.00	
cis		0.074	2.14		
	0.02				4.75
trans		0.074		2.61	
cis		0.030	1.74		
	0.01				3.47
trans		0.031		1.83	

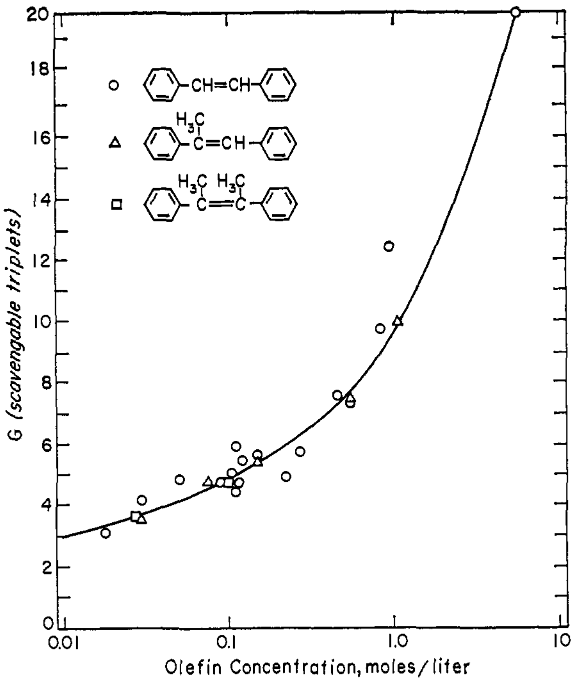

Figure 2. Comparison of triplet yields from different olefins: ○, stilbenes; △, 1,2-diphenylpropenes; □, 2,3-diphenyl-2-butene.

Although an alternative explanation can be used to accont for the behavior of the stilbenes,[13] we believe that the evidence strongly favors the view that the behavior of *trans*-stilbene is anomalous. Previous work has shown that the stationary states established in both direct and sensitized photoisomerization of the stilbenes depend upon initial concentrations.[10] The phenomenon was attributed to "self-quenching" of triplets by *trans*-stilbene. We have also found that excited singlet states of *trans*-stilbene suffer similar self-quenching.[14] Consequently, we believe that the yields in any isomerization that depends on electronic excitation of *trans*-stilbene will fall off when the concentration of the substrate is raised.

No such self-quenching has been observed in photoisomerization of *cis*-stilbene. Consequently, the values of $G_{c,t}$ for *cis*-stilbene provide a measure of the number of *cis*-stilbene molecules that are excited to triplet states if we make the assumption that G_T is given by $G_{c,t} \times 2.4$. Figure 2 shows a plot of the data for G_T calculated from the data gathered from *cis*-stilbene along with those obtained with the diphenylpropenes and *trans*-2,3-diphenyl-2-butene. Data for the latter system were determined in the following manner: a radiostationary state of 52% *trans* was measured from long-term irradiation of solutions of *trans* and *cis–trans* mixtures. *G* values were determined for isomerization of *trans*- to *cis*-2,3-diphenyl-2-butene only. G_T values were determined by applying the decay ratio determined from the stationary-state measurements. Since all three acceptors are expected to quench benzene triplets at the diffusion-controlled rate, they should all give the same value for G_T at low concentrations where most of the energy is absorbed by the solvent. The results show excellent agreement among the three acceptors; *G* is about 6 for benzene triplets scavenged by 0.28 molar acceptor and about 3.5 for 0.03 molar acceptor. In addition, the data gathered for the diphenylpropenes at high concentrations appear to be in good agreement with the values obtained using high concentrations of *cis*-stilbene, even though data gathered with *trans*-stilbene seem to indicate much lower values of G_T.

The mechanism formulated above is not necessarily complete, even if our interpretation of the data is correct. Some of the excited triplets of the scavengers may not have been formed by transfer of triplet excitation from the solvent. Excitation originally delivered to the solute molecules in other forms, such as singlet excitation, as positive charges or as electrons, could be degraded subsequently to triplet energy. The only way in which we can envision ionic species as being important is as precursors of triplet states; there is indeed some analogy for the production of electronically excited species upon neutralization of charge in other systems.[15] A mechanism for the radiolysis of aliphatic hydrocarbons proposed by Dyne[16] involves initial production of both excited states and ionic species, with recapture of electrons by positive ions eventually producing more excited states; we would have no objection to including such a feature in our mechanism.

(13) R. R. Hentz, D. B. Peterson, S. V. Srivastava, H. F. Barzynski, and M. Burton, unpublished manuscript.

(14) D. Valentine, unpublished studies of the self-quenching of fluorescence from *trans*-stilbene.

(15) E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

(16) P. J. Dyne, *Can. J. Chem.*, **43**, 1080 (1965).

The differences between the results of Cundall[9] and our results provide insight into the features of decay of benzene triplets in γ radiolysis. Cundall's[9] plots of G(isomerization) of 2-butene against concentration are concave downward while our curves are concave upward. Moreover, the triplet yield, measured by the sum $G_{t,c}$ plus $G_{c,t}$, is always lower when measured by 2-butene isomerization than when measured by stilbene or 1,2-diphenylpropene isomerization at similar concentrations. Isomerization of 2-butene shows good linear behavior for a plot of $1/G$(isomerization) against 1/[2-butene] (Stern–Volmer plot); data such as those in Table II give curved Stern–Volmer plots.

We can account for the discrepancy only by assuming that, at the concentrations employed in our work, the homogeneous kinetics assumptions involved in making Stern–Volmer plots do not apply and that modifications of eq 4 are necessary. Reactions 4a–c provide a scheme for disposing of benzene triplets in a process higher than first order, as our data require. Such reactions presumably occur within a spur, or small region, in which the initial concentration of primary excited products (ions, excited states, etc.) is high;

$$(C_6H_6)^3 + (C_6H_6)^3 \longrightarrow (C_6H_6)^1 + (C_6H_6)^0 \tag{4a}$$

$$(C_6H_6)^3 + (C_6H_6)^3 \longrightarrow (C_6H_6)^3 + (C_6H_6)^0 \tag{4b}$$

$$(C_6H_6)^3 + (C_6H_6)^3 \longrightarrow 2(C_6H_6)^0 \tag{4c}$$

annihilation (reactions 4a–c) would compete with diffusion out of the spur, and the number of triplets per spur available for transfer to an olefin would depend markedly upon how long the spur had been in existence. The situation is formally analogous to radical–radical coupling in competition with radical scavenging in aqueous solution, for which various inhomogeneous kinetic models have been used with rather good success.[17–20]

The differences between the butenes and the olefins studied in this work can be understood, at least qualitatively, if butenes, at the concentrations employed, scavenge solvent triplets only relatively slowly. The bimolecular $(C_6H_6)^3$–$(C_6H_6)^3$ annihilation would then reduce the number of triplets available for quenching in the butene experiments. If energy transfer to the stilbenes and 1,2-diphenylpropenes is, on the other hand, fast enough to compete with bimolecular decay of benzene triplets, the latter compounds should scavenge more triplets than the butenes. The Stern–Volmer plot for the butene data can be linear only if quenching by butene begins to become important only after $(C_6H_6)^3$ is homogeneously distributed, *i.e.*, after the annihilation reaction has become negligible. Rate constants for transfer of triplet energy from $(C_6H_6)^3$ to 2-butenes may be extracted from Cundall's data.[9b,c] They appear to be about an order of magnitude slower than the diffusion-controlled rate constants we expect for transfer to stilbene and 1,2-diphenylpropene. For transfer to *cis*-2-butene, the rate constant is about 1×10^9 l. mole^{-1} sec^{-1}, while to *trans* it is about 5×10^8.

Our experiments suggest that the yield of triplet benzene plus triplet states of solute is considerably higher than the $G = 4.3$ of Cundall[9c] and the $G \sim 1$–1.4 of other workers.[3,7,8] We feel that the lower values reflect scavenger concentrations too low to intercept all the triplets[3,7,8] or scavengers that are relatively inefficient.[9] To establish the total yield of triplets would require either solute concentrations so high as to make extensive correction for direct absorption of energy by the solute necessary (see Table II for typical data on electron fraction of solute at various concentratins), or would require fitting G(isomerization) data to some theoretical curve; *e.g.*, the diffusion–treatment of Kuppermann.[20] The latter approach neccessarily involves a complex mechanism with first- and second-order terms for triplet benzene disappearance, with further production of triplets by intersystem crossing of benzene singlets produced by annihilation, and with perhaps some kinetic terms for ion recombination. We have not attempted such an analysis in detail. To do so would probably be unjustified, since we do not really know rate constants for critical energy-transfer processes. To assume that k_2 and k_3 can be assigned the diffusion-limited values may be unrealistic for the high concentration situation in which an arbitrarily chosen molecule is likely to have a scavenger molecule as one of its nearest neighbors.[21] Under such circumstances the rates of energy transfer should probably be described by both "short-time" and "long-time" rate constants,[22] with the first being characteristic of transfer rates between molecules already in contact. Our data indicate that the rate constants for transfer to *cis*-stilbene and the *cis*- and *trans*-diphenylpropenes remain approximately equal even under conditions where diffusion is not involved.

Since some of the energy is absorbed directly by the solutes, irradiation of an isomerizable olefin in neat form was of interest. *cis*-Stilbene, being a liquid, is convenient to use, and the products of such irradiation are still only *trans*-stilbene ($G = 8.2$) and phenanthrene ($G =$ *ca.* 0.1). The decay ratio for stilbene triplets gives a value of $G_T = 20$, a value close to that extrapolated from the empirical curve in Figure 2. The implications of the higher values of G_T obtained by direct absorption of energy by the stilbenes and 1,2-diphenylpropenes are that energy-wasting reactions 4a–c are less important for these substances than for benzene. This is entirely reasonable since triplets from stilbene and related compounds are believed to have fast rates of nonradiative decay.[10] The G_T of 20 corresponds to an energy requirement of 5.0 ev/molecule, which is substantially lower than the ionization potential for *cis*-stilbene (*ca.* 8 ev). In kcal/mole, the energy requirement for triplet formation from *cis*-stilbene by γ radiolysis is 115.5; the spectroscopic triplet has an excitation energy of about 57 kcal/mole, so this corresponds to an efficiency of triplet formation of about 49%.

In conclusion, we believe that a large fraction of the energy delivered to the system ultimately appears in the scavenging solutes as triplet excitation. We have constructed a kinetic model in which a key step is

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(18) H. A. Schwarz, *J. Am. Chem. Soc.*, 77, 4960 (1955).

(19) A. Kuppermann in "Actions Chimiques et Biologiques des Radiations," M. Haissinsky, Ed., Vol. 5, Maisson et Cie, Paris, 1961, p 85.

(20) (a) A. Kuppermann and G. G. Belford, *J. Chem. Phys.*, **36**, 1412 (1962); (b) *ibid.*, **36**, 1427 (1962).

(21) H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1911 (1964).

(22) R. M. Noyes, *J. Phys. Chem.*, **65**, 763 (1961).

transfer of triplet excitation from solvent to solute; other models for excitation transfer can be adapted to fit the kinetic observations but seem over-all to be less attractive to us at this time.

Experimental Section

Materials. Samples of purified *trans*- and *cis*-1,2-diphenylpropene were generously supplied to us by Professor D. J. Cram and Dr. D. H. Hunter and were used without further purification. The purification of the stilbenes used in this work has been described.[10] *trans*-Piperylene was obtained from technical grade piperylene by preparative vapor phase chromatography. Reagent grade benzene proved sufficiently pure for these studies.

Radiolyses. Solutions (1-4 ml) of the appropriate substrate in benzene were prepared, degassed, and irradiated in sealed Pyrex 13 × 100 mm tubes. Some initial experiments were performed on undegassed samples with little difference in short-term runs with concentrations of scavengers greater than 0.02 *M*. Irradiations were carried out in a Co^{60} cavity source.[23] Dosimetry (Fricke, $G =$ 15.5) was carried out in similar Pyrex tubes, open to the air. The dose rate (corrected for absorption by the organic solvent and solute) was approximately 2.7×10^{19} ev g^{-1} hr^{-1}. Conversions in the *cis–trans* isomeric systems were carried to 5-50% of completion. Stationary states were usually obtained after irradiating dilute (*ca.* 0.02 *M*) solutions until a total dose of $3\text{-}6 \times 10^{21}$ ev (120-hr duration) had been absorbed.

Analyses were performed by vapor phase chromatography. An internal standard was added to the sample after irradiation, and measurement of relative peak areas gave the amount of each solute present after irradiation, when the usual detector response correction was made.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1479. We are grateful to Professor Aron Kuppermann for valuable discussion and to Professor Burton and Dr. Hentz for the opportunity to examine their data in prepublication form.

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[23] We are indebted to Dr. James King and The National Aeronautics and Space Administration for the use of the source at the Jet Propulsion Laboratory, Pasadena, Calif.

The Structure of the Solvent Shells of Electrons.
I. Hexamethylphosphoramide

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Abstract: Electrons are solvated by hexamethylphosphoramide in such a way that there are four equivalent nearest neighbor solvent molecules, tetrahedrally arranged, with P^{31} contact hyperfine splittings of 4.91 gauss and six next-nearest neighbor solvent molecules, octahedrally arranged, with P^{31} splittings of 1.83 gauss. All of the 35 lines of the epr spectrum to be predicted for such a ten-molecule complex have been found, in the expected intensity ratios. The *g* value, line widths, and splittings of the solvated electron spectrum are independent of the cation, Li^+, Na^+, or K^+, present in the solution. At high concentrations of alkali metals, other unidentified paramagnetic species predominate in the solution.

Alkali metals dissolve or appear to dissolve in a variety of liquids of high dielectric constant such as ammonia, amines, or ethers to give blue solutions. In the case of the ethers dimethoxyethane and tetrahydrofuran, the blue solutions of potassium were found to be diamagnetic.[1] In the better known case of metal–ammonia solutions, strong epr signals are obtained.[2] Pollak[3] showed that the electron relaxation times are longer in $N^{15}H_3$ solutions than in $N^{14}H_3$ solutions. This is indirect evidence of a weak contact hyperfine interaction of the unpaired electron with the nitrogen nuclei of the solvent molecules surrounding the electron.

In 1961 G. Stork and D. R. Coulson at Columbia University observed the blue color of solutions of alkali metals in hexamethylphosphoramide [tris(dimethylamino)phosphine oxide], $([CH_3]_2N)_3PO$, and it was suggested that we make an epr study of these solutions. Subsequently a single epr signal was detected in these solutions.[4]

Experimental Section

The conventional Varian V-4500 X-band epr spectrometer was used, with a V-4013A magnet suitable for high-resolution nmr experiments. When necessary the field was modulated at 400 Hz, as well as 100 kHz, to rule out possible modulation side bands. The hexamethylphosphoramide was obtained distilled from Dow Chemical Co. The solutions were degassed by repeated freezing and evacuation at 10^{-5} mm and lower.

Line intensities were determined from the derivative of the absorption spectrum by utilizing the relation

$$\int_{-\infty}^{\infty} f(B)\,dB = \left|\int_{-\infty}^{\infty} Bf'(B)\,dB\right| \qquad (1)$$

where *B* is the difference in gauss between the field value and the center of the line, and $f'(B)$ is the ordinate of the recorder trace. A typical line was subdivided into 20 or more parts, and the quantity $Bf'(B)$ was summed over all of the line visible above the noise.

Magnetic fields were measured by the proton magnetic resonance method, using a Hewlett-Packard 5245L counter. The microwave

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[2] C. H. Hutchison and R. C. Pastor, *ibid.*, **21**, 1959 (1953); T. P. Das, *Advan. Chem. Phys.*, **4**, 303 (1962).

[3] V. L. Pollak, *J. Chem. Phys.*, **34**, 864 (1961).

[4] G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Am. Chem. Soc.*, **87**, 1406 (1965).