The anticipated rate of I relative to 2,2-dimethylcyclopropylcarbinyl 3,5-dinitrobenzoate is unclear because of the simultaneous operation of uncertain strain and inductive effects associated with the bridgehead methines in I. However, the rates of II and III relative to I can be estimated with more certainty because these effects are relatively constant. The calculation uses the rate enhancement of syn and anti double bonds in 7-substituted norbornenes relative to the saturated 7 derivative[15] combined with the observation that sufficient charge is developed at C_2 in cyclopropylcarbinyl solvolyses to produce one-fifth of the 10^5 methyl rate enhancement found in comparing secondary and tertiary solvolyses.[5,16] Taking the rate of I as 1.0 the expected[17] rate of II is $10^{3.7/5} = 10^{0.74} = 8.7$ and the expected rate of III is $10^{11.1/5} = 10^{2.2} = 160$.

The observed rate data are presented in Table I along with data for the appropriate reference compounds. It is apparent that the expected rate enhancements by the double bond are unambiguously absent. Thus in yet another σ delocalized transition state a resonance stabilizing group fails to provide the rate enhancement that would have been anticipated on the basis of enhancements afforded by methyl substituents. In the present example there is no question of steric inhibition of resonance. The blend of resonance and inductive influence of the remote double bond is markedly different from that presented by a phenyl substituent. It seems inescapable that an appeal to a fortuitous balance of resonance and induction is unacceptable.

The present solvolyses cannot distinguish between the proposal that resonance stabilizing groups are ineffective at stabilizing σ-delocalized ions and the Brown null hypothesis that in cyclopropylcarbinyl there is no delocalized charge to be stabilized. Acceptance of the latter, however, then requires a separate explanation for the rate enhancements arising from methyl substitution. A detailed discussion of such possibilities will be presented elsewhere.

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(14) The syn and anti assignments were made on the basis of the synthetic path and were largely confirmed by an ir study of the alcohols. A single inconsistency in the latter results leaves open the possibility that the assignments of II and III should be reversed. As described later in the text the main thrust of the argument is not affected by the assignment.

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Zero-Field Transitions of Triplet Excimers from Phosphorescence–Microwave Double Resonance Spectroscopy

Sir:

Since the first reported detection of excimer fluorescence in concentrated pyrene solutions,[1,2] evidence has been accumulating which indicates that excimer emission from many aromatic molecules can be observed provided the right conditions of temperature, pressure, and concentration are met.[3] Initially the excimer binding energy was interpreted as arising from either an excitation resonance[4,5] or a charge resonance[6] between the monomers. However, models[7-9] taking into account the configuration interaction between exciton resonance and charge resonance states were found to come much closer to correctly interpreting the magnitude of the experimentally observed red shift of the excimer emission relative to the monomer emission.

Conclusive evidence of the existence of stable triplet excimers is of considerable theoretical interest. Recently, excimer phosphorescence was reportedly observed in several molecules including halogenated benzenes,[10-12] phenanthrene,[13] naphthalene,[13] and pyrene.[14] For triplet excimers, the coulombic terms of the excitation resonance interaction vanish due to spin orthogonality, leaving only the relatively small exchange terms. The contribution of charge resonance interactions, resulting from mixing charge-transfer functions[8] with triplet wave functions of the dimer, might then become the important factor leading to the stability of triplet excimers.

Using phosphorescence–microwave double resonance (PMDR) techniques,[15] the zero-field (zf) transitions of the triplet state of the monomer or of the excimer of hexachlorobenzene (HCB) at 1.6°K could be observed by monitoring the sharp phosphorescence bands of the monomer or the broad excimer emission, respectively. The results show that the broad emission has zero-field transitions and thus confirms its origin as a triplet state. Furthermore, it is found that the excimer of HCB at 1.6°K is formed only at crystal defects that are created by introducing small amounts of other chlorobenzenes whose lowest triplet states are at higher energies than that of HCB. A qualitative comparison of the *D* and *E* values of the excimer and the monomer is made in terms of the excimer structure as well as the charge-transfer mechanism of its stabilization.

Hexachlorobenzene (HCB), *sym*-tetrachlorobenzene (TCB), 1,3,5-trichlorobenzene (Tri-CB), and *p*-dichlorobenzene (DCB) were recrystallized four times from CCl_4, zone refined for 50 passes under nitrogen atmosphere, and chromatographed over Al_2O_3. Samples of pure HCB, HCB doped with 1.0×10^{-3} *M* of TCB, Tri-CB, and DCB were prepared and sealed in quartz ampoules under helium atmosphere and were placed inside a copper helix with the proper characteristics for the desired microwave frequency. The 3130-Å band of a

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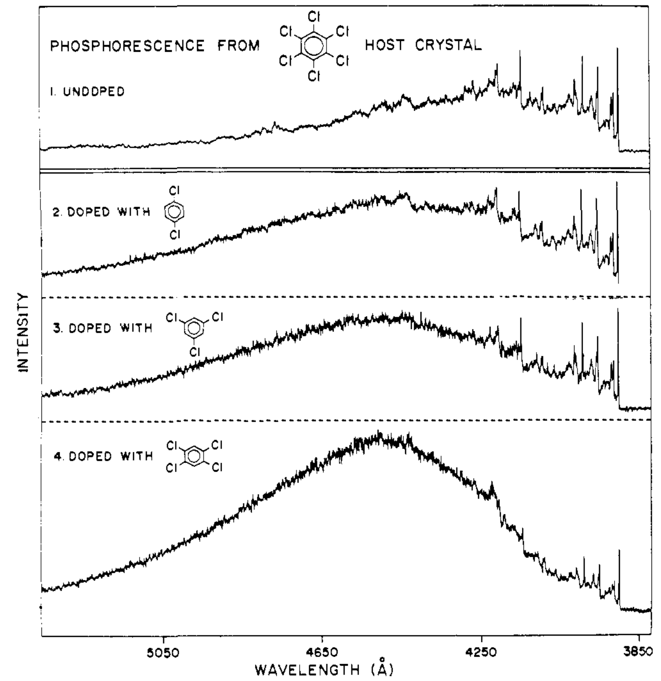

Figure 1. The phosphorescence spectra at 1.6°K of the hexachlorobenzene (HCB) crystal undoped and doped with different chlorobenzenes whose lowest triplet states are higher in energy than that for HCB. The sharp emission is that for HCB monomer while the broad emission in the doped crystals is that for the HCB excimer.

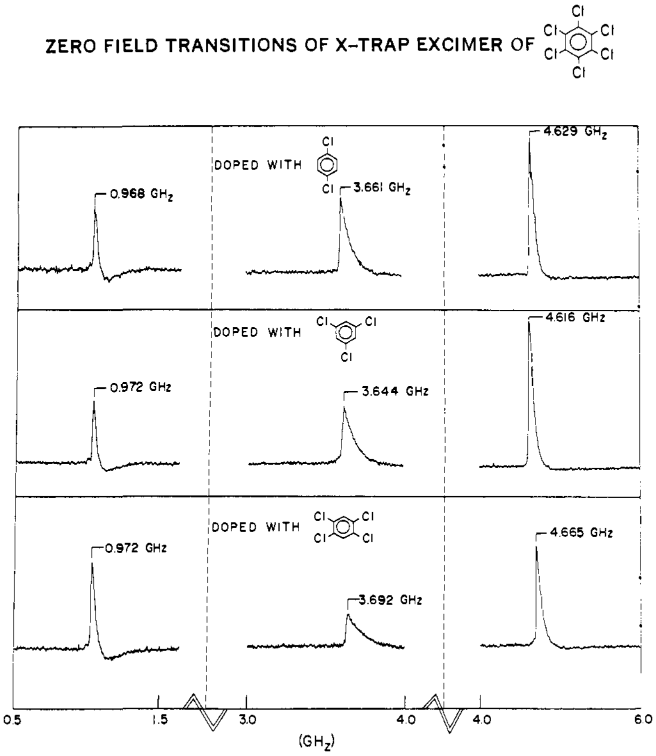

Figure 2. The optically detected zero-field spectra of hexachlorobenzene (HCB) excimers induced by doping the HCB crystal with 1,4-dichlorobenzene (top), 1,3,5-trichlorobenzene (middle), and 1,2,4,5-tetrachlorobenzene (bottom). The spectra are obtained by monitoring the broad emission while sweeping the microwaves. The sweep time of the different spectra is 560 m/sec. Since the sweep time across the band is shorter than the decay times, the band shapes shown do not correspond to true band shapes. The shape of the high-frequency side of each peak gives the lifetime of the radiating zf level(s) whose population has been affected by the microwave pumping. The spectra taken in this manner show that the excimers formed by the different added quests all have the same zf transitions as well as zf lifetimes.

PEK 100-W high-pressure mercury lamp was isolated using 5 cm of an aqueous solution of $NiSO_4$ (150 g/l.) with a U.G.-11 Jenaer glass filter used to excite the sample. The source of microwaves was a Hewlett-Packard 8690B sweep oscillator with associated plug-ins. The microwaves were conducted to the helix *via* a coaxial line and all the experiments were carried out at 1.6°K. The phosphorescence spectrum was recorded using a 1-m Jarrell-Ash spectrometer. The signal representing the change in the phosphorescence intensity upon microwave saturation (PMDR signal) was fed into an NS-560 CAT system with dwell time of 2.5 m/sec per channel.

In Figure 1, the sharp spectrum is that of HCB x traps.[16] These are HCB molecules located next to an impurity molecule whose lowest triplet state is higher in energy than that for HCB. The presence of the impurity molecule lowers the triplet energy of the surrounding HCB molecules. These HCB molecules thus act as traps for the triplet excitons of HCB.

In the undoped HCB crystals, only the x-trap phosphorescence is observed (top spectrum). The optically detected microwave signals observed while monitoring any portion of this spectrum are those for HCB x traps.[17] Only when the HCB crystal is doped with chlorobenzene guest molecules, *e.g.*, DCB (second spectrum), Tri-CB (third spectrum), or TCB (bottom spectrum), does a red-shifted broad excimer type emission appear. This result eliminates the possibility that the broad emission is due to host impurity or host photodecomposition product. At first it was thought that the broad emission might be due to exciplex emission (*i.e.*, from excited dimer of HCB with the added guest molecules). This possibility was eliminated from the results of Figure 2 which show that the position and band shape [whose high-frequency side measures the lifetime of the radiative zf level(s)] of the three microwave spectra for each doped HCB crystal are independent of the kind of guest added. When the PMDR spectra are obtained at low sweep rates, ^{35}Cl and ^{37}Cl hyperfine structure is resolved. These spectra, too, are independent of the type of the added guest molecules. These results might eliminate the possibility that the broad emission is due to an impurity in the added guest or to a photochemical product between HCB and the added guest. The results suggest that the added guest creates centers of crystal defects in which the HCB molecules find themselves in a better stereochemical orientation for the formation of the stable excimer. The possibility that the broad emission is from photochemical products between HCB molecules themselves formed at point defects created by the added guests can also be eliminated by the fact that the intensity of the broad emission is independent of the irradiation time.

The fact that no exciplex PMDR signal was detected could easily be explained by the fact that around

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each impurity there are a number of "defected" HCB molecules. Thus, the probability of forming an excimer is higher than that for an exciplex. In addition, even if an exciplex is formed, it is readily quenched at 1.6°K by the formation of the *lower energy* excimer due to the presence of many neighboring "defected" HCB molecules. It can thus be concluded that, at low temperatures, exciplex emission in this type of crystal could only be observed if the guest added has a lower T_1 energy than that for the host. This is probably the case for the unpurified, undoped HCB crystal which shows broad emission with different microwave spectra than those shown in Figure 2.

The crystal structure of HCB indicates[18] that the distance between equivalent molecules (*i.e.*, molecules in adjacent unit cells) is smaller than that between the inequivalent molecules (*i.e.*, the two molecules in the same unit cell). One might then assume that excimer formation occurs between the equivalent molecules, with their molecular planes being parallel to one another. With this structure, the $|D|$ and $|E|$ values of the monomer are 6.44 and 0.89 GHz, while those for the excimer are 4.151 and 0.485 GHz. A reduction of $|E|$ by 46% could be explained by rotation of one molecule with respect to the other around the axis normal to the two molecular planes. A reduction of $|D|$ by 55% could be explained by one of three possibilities: (1) the molecular planes of the two molecules in the excimer are not exactly parallel; (2) the $|D|$ value of HCB molecules in the excimer changes from its value in the x traps; (3) the charge transfer between one molecule and the other, giving rise to the excimer stability, also separates the two unpaired electrons of the triplet state. This would lead to a decrease in the interelectron dipolar repulsion and would reduce the $|D|$ value.

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Kinetic Study of Radical Production in the Thermal Decomposition of Benzoyl Peroxide by Electron Spin Resonance Spin Trapping (Spin Counting). Rate (and Substituent Effect on the Rate) of Spin Trapping by Competitive Scavenging of Benzoyloxy Radicals with Galvinoxyl

Sir:

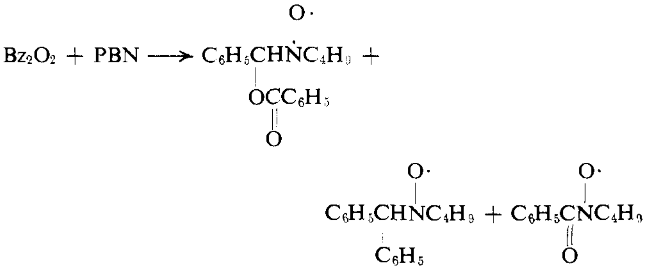
Recent use has been made of a nitrone radical addition reaction[1] to develop a method for the detection and identification of certain short-lived free radicals at concentrations too low for direct esr detection[2,3] (spin trapping). Phenyl *N-tert*-butylnitrone has been most generally useful

$$\mathrm{R\cdot} + \underset{\text{spin trap}}{\mathrm{C_6H_5CH{=}N(O)C(CH_3)_3}} \longrightarrow \underset{\text{spin adduct}}{\mathrm{C_6H_5CH(R)N(O\cdot)C(CH_3)_3}}$$

The β-hydrogen and nitrogen hyperfine splittings of the nitroxides produced are found to be characteristic for a large number of different radicals trapped.

Of obvious interest are the possible quantitative applications of this technique, for example, in counting the number of radicals produced (sometimes of different structure) by a given radical source as a function of time (spin counting). This method has an advantage over presently used methods in that the identity of the radicals produced is known as a function of a given variable. The requirement that both the spin trap and the spin adduct do not induce free-radical production must of course be met.

Benzoyl peroxide was chosen to test this possibility. The esr spectrum obtained from benzoyl peroxide (Bz_2O_2) and phenyl *N-tert*-butylnitrone (PBN) in benzene at room temperature consists of three doublets and has previously been assigned to the benzoyloxy spin adduct[2] (BzO-SA). Both the phenyl spin adduct (Ph-SA) and benzoyl *tert*-butyl nitroxide are also detected although at lower concentrations (usually totaling to not more than 10% of all radicals present depending on reaction conditions).



$$\mathrm{Bz_2O_2} + \mathrm{PBN} \longrightarrow \mathrm{C_6H_5}\underset{\substack{|\\ \mathrm{O}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{C_6H_5}}}{\mathrm{CH}}\overset{\mathrm{O\cdot}}{\mathrm{N}}\mathrm{C_4H_9} + \mathrm{C_6H_5}\underset{\substack{|\\ \mathrm{C_6H_5}}}{\mathrm{CH}}\overset{\substack{\mathrm{O\cdot}\\ |}}{\mathrm{N}}\mathrm{C_4H_9} + \mathrm{C_6H_5}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\overset{\substack{\mathrm{O\cdot}\\ |}}{\mathrm{N}}\mathrm{C_4H_9}$$

A plot of [BzO-SA] as a function of time is linear for 5–15 min[4] at 32–48° when [PBN] = 0.001–1 *M* for [Bz_2O_2] = 0.1 *M* and [Bz_2O_2] = 0.05–0.5 *M* for [PBN] = 0.1 *M* in benzene. Rates obtained from these initial slopes show that BzO-SA production is first order in Bz_2O_2 and almost zero in PBN for [PBN] > 0.075 *M*. At low concentrations of PBN the order in PBN is higher although initial rates are not linear for sufficient lengths of time for accurate determinations. These results are consistent with an essentially noninduced radical scavenging mechanism for PBN spin trapping, where the rate of trapping is much faster than the rate of thermal decomposition of benzoyl peroxide.

$$\mathrm{Bz_2O_2} \longrightarrow 2\mathrm{BzO\cdot} \tag{1}$$

$$\mathrm{BzO\cdot} + \mathrm{PBN} \longrightarrow \mathrm{BzO\text{-}SA} \tag{2}$$

As expected, decarboxylation of benzoyloxy radicals competes with addition to PBN. The phenyl radicals either are trapped by PBN or solvent.

$$\mathrm{BzO\cdot} \longrightarrow \mathrm{Ph\cdot} + \mathrm{CO_2} \tag{3}$$

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