

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 indicates¹⁸ 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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(18) A. Tulinsky and J. G. White, *Acta Crystallogr.*, **11**, 7 (1958).

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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:

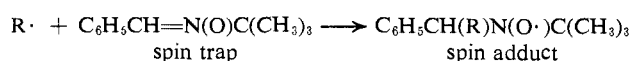
Recent use has been made of a nitron radical addition reaction¹ to develop a method for the detection and identification of certain short-lived free radicals at concentrations too low for direct esr detection^{2,3} (spin trapping). Phenyl *N-tert*-butylnitron has been most

(1) M. Iwamura and N. Inamoto, *Bull. Chem. Soc. Jap.*, **40**, 702, 703 (1967); **43**, 856, 860 (1970).

(2) E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **90**, 5909 (1968); **91**, 4481 (1969).

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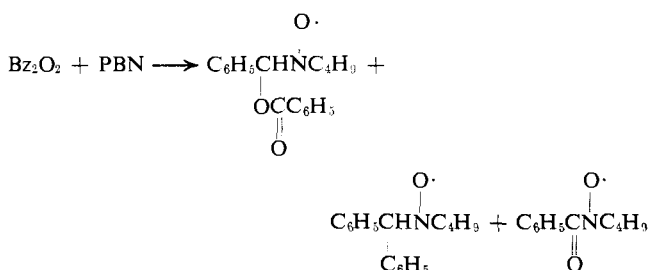
generally useful



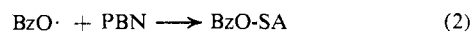
The β -hydrogen and nitrogen hyperfine splittings of the nitroxides produced are found to be characteristic for a large number of different radicals trapped.

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.

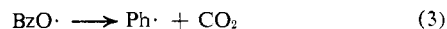
Benzoyl peroxide was chosen to test this possibility. The esr spectrum obtained from benzoyl peroxide (Bz_2O_2) and phenyl *N-tert*-butylnitron (PBN) in benzene at room temperature consists of three doublets and has previously been assigned to the benzoyloxy spin adduct² ($\text{BzO}\cdot\text{SA}$). Both the phenyl spin adduct ($\text{Ph}\cdot\text{SA}$) 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).



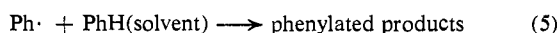
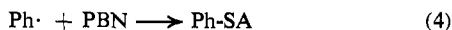
A plot of $[\text{BzO}\cdot\text{SA}]$ as a function of time is linear for 5–15 min⁴ at 32–48° when $[\text{PBN}] = 0.001\text{--}1\text{ M}$ for $[\text{Bz}_2\text{O}_2] = 0.1\text{ M}$ and $[\text{Bz}_2\text{O}_2] = 0.05\text{--}0.5\text{ M}$ for $[\text{PBN}] = 0.1\text{ M}$ in benzene. Rates obtained from these initial slopes show that $\text{BzO}\cdot\text{SA}$ production is first order in Bz_2O_2 and almost zero in PBN for $[\text{PBN}] > 0.075\text{ M}$. 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.



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



(4) The first two peaks of the spectrum are scanned repeatedly at 30-sec intervals for the first 10–20 min of the reaction. The peak heights are converted to area units according to a double integration formula (C. P. Poole, "Electron Spin Resonance," Interscience, New York, N. Y., 1967, p 784 ff). Area units are calibrated by the use of the stable nitroxide, 2,2,5,5-tetramethylpyrrolidine nitroxide-3-carboxamide available from Frinton laboratories. Peak overlap effects of $\text{BzO}\cdot\text{SA}$ and $\text{Ph}\cdot\text{SA}$ are taken into account by computer simulation of summed spectra.



Of interest here is the determination of k_1 from spin trapping to compare with literature values. These rate constants are obtained from the following expression⁵ at different temperatures and are listed in

$$d[\text{BzO-SA}]/dt = 2k_1[\text{Bz}_2\text{O}_2][\text{PBN}]/([\text{PBN}] + k_3/k_2)$$

Table I, along with literature values at higher tempera-

Table I. Rate Constants of the Thermal Decomposition of Benzoyl Peroxide in Benzene

	k_1, sec^{-1}	Temp, °C	Ref
1.	$(3.7 \pm 0.2) \times 10^{-8}$	38 ^a	This work
2.	$(5.0 \pm 0.2) \times 10^{-8}$	39 ^a	This work
3.	$(6.4 \pm 0.3) \times 10^{-8}$	40 ^a	This work
4.	$(1.1 \pm 0.1) \times 10^{-7}$	44 ^a	This work
5.	$(1.9 \pm 0.1) \times 10^{-7}$	48 ^a	This work
6.	4.24×10^{-7}	50.8	7
7.	8.52×10^{-7}	54.9	7
8.	1.94×10^{-6}	60	8
9.	1.66×10^{-6}	60.9	7
10.	3.22×10^{-6}	65.6	7
11.	5.96×10^{-6}	71.0	7
12.	1.19×10^{-5}	75.8	7
13.	1.88×10^{-5}	78	9
14.	1.67×10^{-5}	78	9 ^b
15.	2.58×10^{-5}	79	10
16.	3.28×10^{-5}	80	8
17.	2.36×10^{-5}	80	11 ^c

^a Temperature controlled to $\pm 0.3^\circ$. ^b Induced decomposition inhibited with galvinoxyl. ^c In chlorobenzene.

tures.⁷⁻¹¹ An Arrhenius plot for the rates obtained by spin trapping gives an activation energy of 30.4 kcal/mol¹² (values of 29-33 kcal/mol have been reported by other workers⁷⁻¹¹). The Arrhenius plot for data from several workers is shown in Figure 1 and gives an energy of activation of 32.8 kcal/mol. The good agreement between the results obtained from spin trapping and previously used radical scavenging methods provides strong support for the usefulness of PBN for spin counting.¹³

From these results the rates of radical trapping by PBN can be estimated. If the value of k_3 is taken as 10^3 - 10^4 sec^{-1} at 40° ,¹⁴ $k_2 = 10^5$ - $10^6 \text{ M}^{-1} \text{ sec}^{-1}$. This rate range seems reasonable because it is close to the

(5) $k_2/k_3 = 123 \text{ M}$ was evaluated from a plot of $d[\text{BzO-SA}]/d[\text{Ph-SA}]$ vs. $[\text{PBN}]$, where $d[\text{BzO-SA}]/d[\text{Ph-SA}] = k_2[\text{PBN}]/k_3 + k_2k_5[\text{PhH}]/k_3k_4$. The fact that this plot gives a nonzero intercept requires an additional competing step like reaction 5 to accommodate the data. According to DeTar⁶ reaction with solvent should be the fastest alternative for phenyl radicals.

(6) D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967).

(7) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

(8) K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, **68**, 1686 (1946).

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(10) G. S. Hammond and L. M. Soffer, *J. Amer. Chem. Soc.*, **72**, 4711 (1950).

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(12) Individual rates and energies of activation were calculated from a linear least-squares treatment. Reproducibility of the rates was $\pm 6\%$.

(13) However, recent studies by R. Konaka, T. Mizuta, and S. Terabe (Annual Meeting of the Japanese Chemical Society, Tokyo, Japan, April 1, 1972) show that PBN induces radical production from *tert*-butyl hydroperoxide and hydrogen peroxide.

(14) k_3 has previously been estimated⁸ to be 10^4 - 10^5 sec^{-1} at 87° . The activation energy for $\text{C}_6\text{H}_5\text{CO}_2\cdot \rightarrow \text{C}_6\text{H}_5\cdot + \text{CO}_2$ has been determined to be 12 kcal/mol; J. C. Bevington and J. Toole, *J. Polym. Sci.*, **28**, 413 (1958).

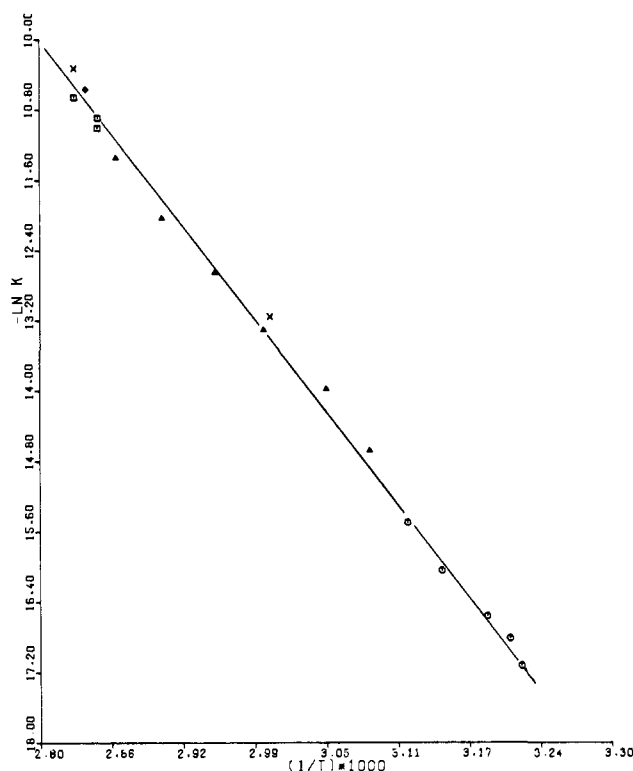
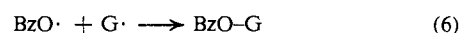


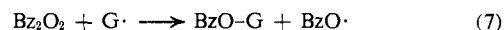
Figure 1. Arrhenius plot for the unimolecular decomposition of benzoyl peroxide: (○) this work; (△) ref 7; (×) ref 8; (□) ref 9 and 11; (◇) ref 10.

value found for the trifluoromethyl radical addition to ethylene in cyclohexane or heptane: $3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$.¹⁵ An estimate of k_5 can be obtained from the intercept of the plot described in ref 5 if we assume $k_2 \approx k_4$; since $k_2k_5[\text{PhH}]/k_3k_4$ is found to be 6, $k_5/k_4 = 0.04$ and $k_5 = 10^2$ - $10^3 \text{ M}^{-1} \text{ sec}^{-1}$. DeTar⁶ has estimated $k_5 = 2 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ at 87° .

An independent evaluation of k_2 is possible from a study of the competitive scavenging of benzoyloxy radicals by galvinoxyl (G) and PBN (eq 6). Thus the



simultaneous decay of G and build-up of BzO-SA can readily be followed by esr in a benzene solution of Bz_2O_2 at room temperature. Preliminary comparisons of these curves indicated that G was much more efficient than PBN in trapping $\text{BzO}\cdot$ radicals. However, it was found that the production of $\text{BzO}\cdot$ radicals in the presence of G is faster than expected based on the known rate of decomposition of Bz_2O_2 at these temperatures. Moreover, considerable curvature is found in the decay plot of G with time in a solution of relatively high concentrations of Bz_2O_2 . Since it is known that Bz_2O_2 decomposition is accelerated by the addition of stable free radicals (e.g., triphenylmethyl¹⁶) an induced decomposition of Bz_2O_2 by G which produces additional $\text{BzO}\cdot$ radicals is a likely possibility



In fact the G decay plot in the presence of Bz_2O_2 is well

(15) R. A. Weir, P. P. Infelte, and R. H. Schuler, *J. Phys. Chem.*, **74**, 2596 (1970); see also J. M. Sangster and J. C. J. Thynne, *ibid.*, **73**, 2746 (1969).

(16) T. Suehiro, A. Kanoya, H. Hara, T. Nakahama, M. Omori, and T. Komori, *Bull. Chem. Soc. Jap.*, **40**, 668 (1967).

fitted by this mechanism¹⁷ with $k_7 = 1 \times 10^{-4} M^{-1} \text{sec}^{-1}$.¹⁸ When reaction 7 is included G is found to be only approximately 50 times more efficient than PBN in trapping $\text{BzO}\cdot$ radicals¹⁹ (see Table II).

Table II. Initial Rate Ratios for Competitive Benzoyloxy Radical Scavenging by Substituted Phenyl *N-tert*-Butylnitrones and $10^{-4} M$ Galvinoxyl

R	[R-PBN], <i>M</i>	(100) k_2/k_6
<i>p</i> -CH ₃ O	1×10^{-3}	4.4
<i>p</i> -CH ₃	5×10^{-3}	3.0
H	5×10^{-3}	1.9
<i>p</i> -Cl	5×10^{-3}	1.4
<i>p</i> -NO ₂	1×10^{-2}	0.86

An estimate of $2 \times 10^7 M^{-1} \text{sec}^{-1}$ for the rate constant of the reaction of methyl radicals with galvinoxyl is available.²⁰ If the same rate constant is assumed for the reaction of $\text{BzO}\cdot$ with G, the rate constant for PBN spin trapping of $\text{BzO}\cdot$ is $4 \times 10^5 M^{-1} \text{sec}^{-1}$. This value compares well with the previous estimate of 10^5 – $10^6 M^{-1} \text{sec}^{-1}$ based on different considerations.

Since the effect of structure and substituents on the rate of reaction 2 is of some interest in spin trapping, data for four para-substituted PBN's have been obtained (see Table II). It is found that electron donation enhances and electron withdrawal hinders the rate of $\text{BzO}\cdot$ addition to PBN but the effect is not large. A Hammett plot fits σ^+ better than σ with a slope of -0.47 . For benzoyloxy radicals one concludes that the transition state has some polar character with PBN the electron donor, since the Hammett slope would be expected to be positive if the substituent effect mainly influences the energy of PBN in the ground state. This result is not unexpected for an electrophilic radical. One might anticipate a less negative slope (maybe positive) for a nucleophilic radical (*e.g.*, hydroxy or alkoxyalkyl radicals) and a negligible substituent effect for phenyl radical additions. Studies of such systems are in progress.

(17) $-d[G]/dt = 2[\text{Bz}_2\text{O}_2](k_1 + k_7[G])$ integrates to $[G\cdot] = (k_1/k_7 + [G\cdot]_0) \exp(-2k_7[\text{Bz}_2\text{O}_2]t) - (k_1/k_7)$.

(18) This value is considerably lower than that for triphenylmethyl radical induced decomposition of Bz_2O_2 : $k = 1.2 M^{-1} \text{sec}^{-1}$ at 25° ;¹⁸ in fact the induced decomposition of Bz_2O_2 by G is slow enough that G has been used⁹ to suppress the "ordinary" induced decomposition of Bz_2O_2 in benzene which always accompanies the simple homolysis in the absence of inhibitors (see K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley, New York, N. Y., 1971, p 151).

(19) The initial rate ratio was obtained at 40° with $10^{-1} M \text{Bz}_2\text{O}_2$, $10^{-2} M \text{PBN}$, and $10^{-4} M \text{G}$; $k_2/k_6 = 0.0193$ was extracted from the following expression where $k_1 = 6.4 \times 10^{-8} \text{sec}^{-1}$ (see Table I).

$$\frac{-d[G]/dt}{d[\text{BzO}\cdot\text{SA}]/dt} = \frac{[G](2k_1k_6/k_2 + 2[G]k_7k_6/k_2 + k_7[\text{PBN}])}{[\text{PBN}](2k_1 + k_7[G])}$$

(20) R. H. Schuler, *J. Phys. Chem.*, **68**, 3873 (1964).

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Excited State $\text{Ru}(\text{bipy})_3^{2+}$ as an Electron-Transfer Reductant

Sir:

It was reported recently that the first triplet charge-transfer state of $\text{Ru}(\text{bipy})_3^{2+}$, where bipy denotes

2,2'-bipyridine, can sensitize substitution reactions of coordination compounds.¹ We describe here results which indicate that this state can also function as an electron-transfer reductant, the complex being oxidized to ground-state $\text{Ru}(\text{bipy})_3^{3+}$.

Our first experiments were carried out with solutions buffered with acetate to pH 4 and $1.25 \times 10^{-4} M$ in $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ and $1 \times 10^{-3} M$ in $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$: such solutions show negligible reaction in the dark. Irradiation at 410 nm led to Co^{2+} production with a quantum yield, ϕ , of 0.1. There was formed no detectable $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ ($\phi \leq 0.001$), free bipyridyl ($\phi \leq 0.001$), or free pyridine ($\phi \leq 0.003$). In fact, no consumption of $\text{Ru}(\text{bipy})_3^{2+}$ occurred, and the process at this point appeared to be one of ordinary photosensitization such as previously reported for cobalt(III) amines.² We were concerned, however, that a chemical mechanism might still be involved, since at pH 4 $\text{Ru}(\text{bipy})_3^{3+}$ is rapidly reduced by solvent. The standard oxidation potential for the $\text{Ru}(\text{bipy})_3^{2+}$ – $\text{Ru}(\text{bipy})_3^{3+}$ couple is -1.23V .³

Reduction of $\text{Ru}(\text{bipy})_3^{3+}$ by solvent is slow in $1 N \text{H}_2\text{SO}_4$, and this medium was tested, using the above concentrations of $\text{Ru}(\text{bipy})_3^{2+}$ and of substrate. There is again no dark reaction, but now on irradiation at 410 nm the initial strong luminescence from $^3\text{Ru}(\text{bipy})_3^{2+}$ fades and the solution changes from yellow to the light green color of $\text{Ru}(\text{bipy})_3^{3+}$. The amount of $\text{Ru}(\text{bipy})_3^{3+}$ formed was determined by following the increase in absorbance at 452 nm as the slow thermal reduction back to $\text{Ru}(\text{bipy})_3^{2+}$ took place following the irradiation. Thus, in one experiment, photolysis to 8% reduction of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ was accompanied by 50% oxidation of the $\text{Ru}(\text{bipy})_3^{2+}$. If the irradiated solution was immediately brought to pH 4 by the addition of sodium acetate, the full original amount of $\text{Ru}(\text{bipy})_3^{2+}$ was regenerated. A series of experiments established the average stoichiometry to be 1.4 Co^{2+} produced per $\text{Ru}(\text{bipy})_3^{2+}$ oxidized. Since the reduction yields Br^- , an ion which rapidly reduces $\text{Ru}(\text{bipy})_3^{3+}$, the resulting Br^- may in part react with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ to increase the apparent yield of Co^{2+} .

There seems to be no doubt that $^3\text{Ru}(\text{bipy})_3^{2+}$ is implicated. Emission from this state is partially quenched on O_2 saturation of the solution: we find a concomitant reduction in $\phi_{\text{Co}^{2+}}$ of about 60%. The triplet state is also quenched by $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, as shown in Figure 1, which yields a Stern–Volmer constant, K_{SV} , of $255 M^{-1}$, a value consistent with the diffusional encounter rate of two dipositive ions. The concentration dependence of $\phi_{\text{Co}^{2+}}$ is given in Figure 2: the least-squares line yields a K_{SV} of $298 M^{-1}$, a value not inconsistent with that from the quenching studies in view of the possibility that the stoichiometry of the reaction may change with concentration.

The mechanism of the reaction appears to be one of electron transfer from $^3\text{Ru}(\text{bipy})_3^{2+}$ to $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ during an encounter. However, it is not possible at this stage to eliminate a mechanism of ordinary photosensitization followed by oxidation of $\text{Ru}(\text{bipy})_3^{2+}$ in

(1) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 1800 (1971).

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(3) D. M. Hercules and F. E. Lytle, *J. Amer. Chem. Soc.*, **88**, 4745 (1966).