Table VII. The Radiolysis of Neopentane in the Presence of Added Ammonia. Yields of Products[a]

	M/N_+		
	0% NH_3	1.5% NH_3	5.0% NH_3
Methane	0.17	0.16	0.16
Acetylene	0.040	0.031	0.031
Ethylene	0.10	0.10	0.098
Ethane	0.069	0.062	0.058
Propane	0.020	0.019	0.021
Propylene	0.081	0.095	0.085
Isobutene	0.30	0.67	0.68

[a] Pressure of neopentane = 40 Torr in all experiments.

the effects of benzene or a graphite surface on the yield of this product are not known at the present time.

Reaction of the *t*-Butyl Ion with Ammonia. Recently Miyazaki and Shida[5] irradiated neopentane in the presence of varying amounts of ammonia. They noted that owing to the occurrence of reaction 24, the yield

$$(CH_3)_3C^+ + NH_3 \longrightarrow (CH_3)_2CCH_2 + NH_4^+ \qquad (24)$$

of isobutene increases markedly upon the addition of even a small amount of ammonia, and becomes constant at higher ammonia concentration. Taking the increment in the isobutene yield as equal to the yield of the *t*-butyl ion, they derived an ion pair yield of 0.42 (G = 1.76), for the *t*-butyl ion in the radiolysis of neopentane at 180 Torr. Table VII gives the yields of products formed in the radiolysis of neopentane–O_2 mixtures in the presence of ammonia; we see that at a pressure of 40 Torr, the increment in the isobutene yield is 0.38.[18]

Taking into account the fact that in the absence of ammonia about 25–30% of the isobutene has the *t*-butyl ion as precursor, we derive a value of 0.47 as the ion pair yield of *t*-butyl ions undergoing reaction 24. Since we have attributed an ion pair yield of 0.67 to the butyl ion formed in the radiolysis of neopentane at this pressure, it is clear that only about 70% of the *t*-butyl ions reacting with ammonia undergoes reaction 24; the remainder in all likelihood undergoes a condensation reaction

$$t\text{-}C_4H_9^+ + NH_3 \longrightarrow C_4H_9NH_3^+ \qquad (25)$$

Taking these corrections into account, the data of Miyazaki and Shida lead to an estimated ion pair yield of ~0.72 for the *t*-butyl ion at 180 Torr, assuming that k_{25}/k_{24} is independent of pressure. This estimated yield is in quite reasonable agreement with the yield of 0.75 at 200 Torr reported above.

Acknowledgment. The authors are indebted to Dr. Abraham Schneider, Research and Development Division, Sun Oil Co., who suggested that the variations in the rate of reaction of the *t*-butyl ion with various alkanes could in many cases be explained in terms of a conformational analysis of the reacting molecules.

[18] Differences between our data and those of Miyazaki and Shida[5] can be explained by the fact that our ammonia additive experiments are performed at a lower pressure (40 Torr). As noted above, the yields of both the *t*-butyl ion and the isobutene not originating from a *t*-butyl ion precursor are pressure dependent over this range.

Reversible Triplet Energy Transfer and Thermally Activated Delayed Phosphorescence

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Contribution from the Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974. *Received December 1, 1969*

Abstract: The lowest triplet states of the benzophenone and triphenylene chromophores in the ester of 2-hydroxymethyltriphenylene and 4-benzoylbenzoic acid in a cured poly(methyl methacrylate) film are in thermal equilibrium over the temperature range 82–298°K. This leads to a temperature-dependent phosphorescence spectrum and triplet decay time for the compound.

Mixed molecular systems of weakly interacting components which possess excited state energy levels lying within an energy range comparable to kT often exhibit strongly temperature-dependent luminescence properties and excitation transfer characteristics.[1-3] We report here on the interesting temperature-dependent luminescence properties of a compound which has two chromophores whose triplet levels lie within about 2 kcal/mol of each other. This represents an intramolecular analog of the mixed crystal experiments of Harrigan and Hirota.[3]

The phosphorescence spectrum of the ester (BT) of 2-hydroxymethyltriphenylene (T) and 4-benzoylbenzoic acid, recorded from a solution in "cured" polymethylmethacrylate near liquid nitrogen temperature, is similar to the sum of the corresponding spectra of T and B, the 4-methylbenzyl ester of 4-benzoylbenzoic acid, in the ratio 2:3, respectively (Figures 1 and 2). However, at room temperature the phosphorescence spectrum of BT resembles that of B. Analyses of the temperature dependences of the phosphorescence spectra, yields, and decay times of BT, B, and T have been carried out. The results fit a model in which triplet excitation transfer back and forth between the two chromophores in BT is sufficiently fast over the temperature range studied

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[1] M. A. El-Sayed, M. T. Wauk, and G. W. Robinson, *Mol. Phys.*, **5**, 205 (1962).

[2] N. Hirota and C. A. Hutchison, Jr., *J. Chem. Phys.*, **42**, 2869 (1965).

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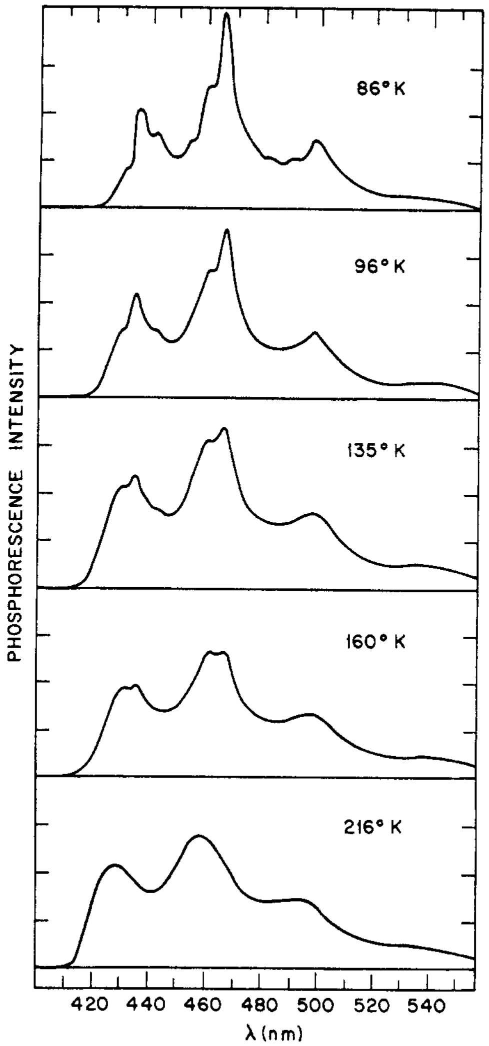
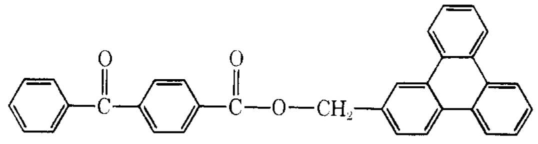
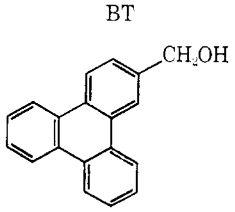


Figure 1. Phosphorescence spectra of BT in poly(methyl methacrylate), excited at 313 nm, recorded at various temperatures.

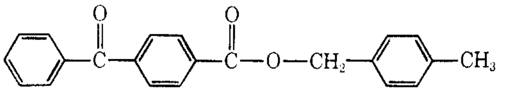
(82–298°K) to maintain thermal equilibrium between the triplet states of the two chromophores.



BT



T



B

Experimental Section

BT was prepared by condensing 2-hydroxymethyltriphenylene and 4-benzoylbenzoyl chloride in pyridine at room temperature (recrystallized from toluene; mp 150–151°, corrected). The 2-hydroxymethyltriphenylene was prepared[4] by reducing 2-triphenylenecarboxylic acid[5] with lithium aluminum hydride (7 days, refluxing ether). B was prepared from 4-methylbenzyl alcohol and 4-benzoylbenzoyl chloride (recrystallized from toluene; mp 67.5–68.5°, corrected).

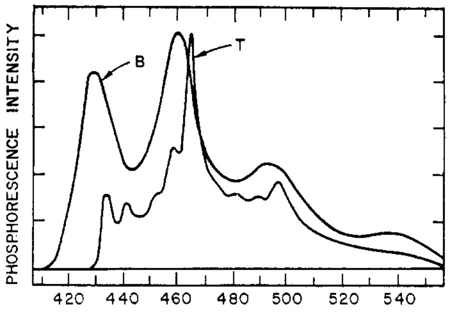


Figure 2. Phosphorescence spectra of B and T in poly(methyl methacrylate) at 80°K, excited at 313 nm.

Samples of B, T, and BT (5×10^{-3} *M*) in poly(methyl methacrylate) were prepared and "cured" according to the procedure of Jones and Siegel.[6] The spectrofluorophosphorimeter used has been described elsewhere.[7] Phosphorescence decay times shorter than 0.1 sec were determined using an oscilloscope in conjunction with the fast shutter.

Results and Discussion

If the interactions in the ground levels and lowest triplet levels between the chromophores in BT are sufficiently weak, then, at equilibrium, the relative populations of triphenylene (t) and benzophenone (b) chromophore triplets in a sample of BT are given by

$$\frac{[\mathrm{b}]}{[\mathrm{t}]} \cong Ce^{-\Delta E/RT} \tag{1}$$

where $\Delta E = E_\mathrm{b} - E_\mathrm{t}$, the difference between the triplet excitation energies of the two chromophores (cal/mol), $R = 1.99$ cal/(mol deg), T is the temperature in degrees Kelvin, and C is related to the densities of levels in the two triplets in the region of interconversion.

The ratio of the intensities, I, of the phosphorescent emissions from the two chromophores in BT at a temperature T is then expected to be

$$\frac{I_\mathrm{B}}{I_\mathrm{T}} = \frac{f_\mathrm{b}k_\mathrm{b}[\mathrm{b}]}{f_\mathrm{t}k_\mathrm{t}[\mathrm{t}]} = \frac{f_\mathrm{b}k_\mathrm{b}}{f_\mathrm{t}k_\mathrm{t}}Ce^{-\Delta E/RT} \tag{2}$$

where k_b and k_t are the decay rates of the triplet states of the isolated triplets and f_b and f_t are the fractions of those decays which are radiative. Equation 2 may be rewritten

$$\ln\left[\frac{I_\mathrm{t}f_\mathrm{b}k_\mathrm{b}}{I_\mathrm{b}f_\mathrm{t}k_\mathrm{t}}\right] + \ln C = \left(\frac{\Delta E}{R}\right)\frac{1}{T} \tag{3}$$

The rate of decay k_BT of the triplet of BT if equilibrium is maintained and $Ce^{-\Delta E/RT} \ll 1$ is

$$k_\mathrm{BT} = k_\mathrm{b}Ce^{-\Delta E/RT} + k_\mathrm{t} \tag{4}$$

which may be rewritten

$$\ln\left[\frac{k_\mathrm{b}\tau_\mathrm{BT}}{1 - \tau_\mathrm{BT}k_\mathrm{t}}\right] + \ln C = \left(\frac{\Delta E}{R}\right)\frac{1}{T} \tag{5}$$

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(4) A. Fry, unpublished results.

(5) J. W. Cook and C.L. Hewett, *J. Chem. Soc.*, 398 (1933).

(6) P. F. Jones and S. Siegel, *J. Chem. Phys.*, **50**, 1134 (1969); Aerospace Corp. Report No. TR-0200(925001)-1.

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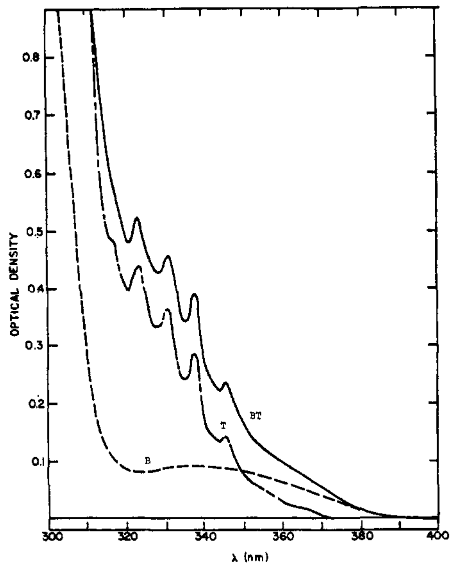

Figure 3. Absorption spectra of B, T, and BT in ethanol at 5 × 10^{-4} *M*.

where

$$\tau_{BT} = 1/k_{BT}$$

In this study it is assumed that over the temperature range of the measurements, B and T are suitable models for the b and t chromophores of BT. This is to say, $k_B = k_b$, $k_T = k_t$, etc.

The lifetime of the phosphorescence of T in cured poly(methyl methacrylate) near liquid nitrogen temperature is about 10 sec, while that of B is about 4 msec. At room temperature the lifetimes are 7 sec and 0.9 msec, respectively. Thus, over the temperature range, $k_B/k_T \sim 10^4$. From the onsets of the phosphorescence spectra one expects $E_B - E_T = \Delta E \sim 2$ kcal/mol, so that $e^{-\Delta E/RT}$ goes from $\sim 10^{-4}$ to $\sim 10^{-1}$ over the temperature range. Thus, if thermal equilibrium between the triplets of the two chromophores in BT can be maintained and C and f_B/f_T are on the order of unity, eq 2 predicts I_B/I_T to be ~ 1 near liquid nitrogen temperature and ~ 10 near room temperature.

The absorption spectrum of BT in ethanol at wavelengths above 300 nm was found to be virtually identical with the sum of the absorption spectra of B and T (Figure 3). Thus there are no strong interactions between b and t in the ground state of BT nor in the low-lying excited singlet states.

A sample of T in poly(methyl methacrylate) gave the fluorescence spectrum ($\varphi_f \cong 0.02$) shown in Figure 4. The fluorescence spectrum of BT excited at 313 nm (80% of the exciting light absorbed by t) is very similar, but the yield is reduced by a factor of about 4. This is most likely due to singlet excitation transfer from t to b, which has a lower singlet level. The transfer appears to be about 65% efficient. Thus with 313-nm excitation 20% of the light is absorbed by b directly and about 55% excites b singlets by way of energy transfer from t. Since b has totally efficient intersystem crossing,[8] the yield of triplets initially formed at b is about 0.75. Intersystem crossing in T is also very efficient ($\varphi_{isc} > 0.9$;[8] also see below), so that the yield of triplets initially formed at t is about 0.25. Excitation of BT with 365-nm light, on the other hand, leads to almost all the intersystem crossing taking place at b.

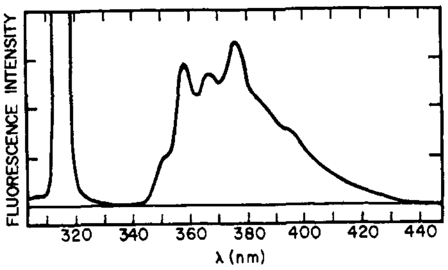

Figure 4. Fluorescence spectrum of T in poly(methyl methacrylate), excited at 313 nm and recorded at room temperature.

The phosphorescence spectra of BT recorded at various temperatures are shown in Figure 1. The spectra were found to be *independent* of the wavelength of the exciting light, which was varied from 290 to 365 nm. Using the spectra of B and T recorded at similar temperatures, the spectra of Figure 1 recorded at 86, 96, and 135°K were resolved into contributions from b and t, and the ratios of the integrated intensities of the components were measured. These are recorded in Table I. It was not possible to obtain accurate data for higher temperatures because the spectra are overwhelmingly B-like at these temperatures. A value of two for the ratio f_B/f_T was obtained from measurements of the phosphorescence yields of B and T in ethanol solution at 82°K. It is assumed that this value obtains for the poly(methyl methacrylate) matrix as well. The ratio f_B/f_T is taken to be constant over the temperature range 82–135°K because the ratio k_B/k_T is nearly constant over this range. Values of k_B and k_T, given in Tables I and II for various temperatures, were obtained by interpolation using curves of lifetimes of B and T *vs.* temperature, in which the experimental points were for different but similar temperatures to those given in the tables.

Table I

Temp, °K	I_t/I_b	f_B/f_T	k_B, sec^{-1}	k_T, sec^{-1}	$\frac{I_t f_B k_B}{I_b f_T k_T}$
86	1.5	2	210	0.093	6.8 × 10^3
96	0.65	2	220	0.095	3.1 × 10^3
135	0.20	2	230	0.098	9.4 × 10^2

Table II

Temp, °K	k_B, sec^{-1}	k_T, sec^{-1}	τ_{BT}, sec	$\frac{k_B\tau_{BT}}{1 - k_T\tau_{BT}}$
82	2.1 × 10^2	0.093	8.6	9.0 × 10^3
98	2.2 × 10^2	0.094	7.4	5.4 × 10^3
116	2.2 × 10^2	0.096	3.5	1.2 × 10^3
150	2.3 × 10^2	0.10	1.2	3.1 × 10^2
166	2.5 × 10^2	0.10	0.80	2.2 × 10^2
214	3.0 × 10^2	0.11	0.36	1.0 × 10^2
293	1.1 × 10^3	0.14	0.017	18

Values for $I_t k_B f_B/I_b k_T f_T$ calculated from the data are given in Table I and are plotted according to eq 3 in Figure 5.

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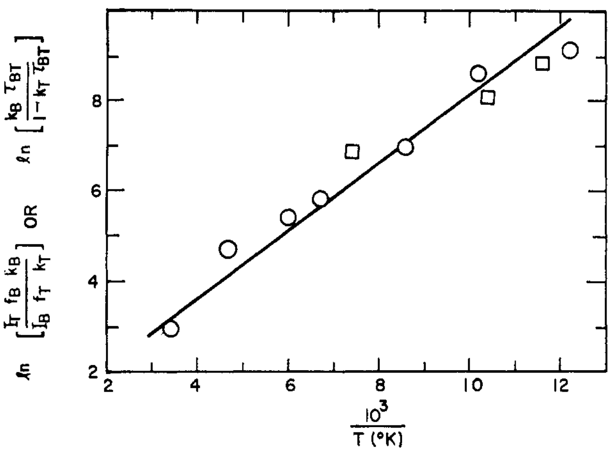

Figure 5. Plot of ln ($I_t f_B k_B/I_b f_T k_T$), □, and ln ($k_B\tau_{BT}/1 - k_T\tau_{BT}$), ○, *vs.* $1/T$. The intercept of the plot (at $1/T = 0$) which is not shown gives ln $C = -0.6$.

The decay of the phosphorescence from BT after exciting to a steady state was recorded at various temperatures. While the decay curves were found to be independent of the wavelength of the exciting light, there was some variation depending on the emission wavelength monitored. Generally, the main component of the decay varied by 10–20%, being shorter at the shorter wavelengths. None of the measured decays was a pure exponential, but each usually could be resolved into two exponentials. The major component (70–90%) was always the faster one. These decay characteristics are probably due to inhomogeneity of environment or conformation in the plastic film. The decay curves recorded from samples in ethanol glass at 80°K were good exponentials. The values of τ_{BT} recorded in Table II were obtained from the major components of the decay curves which were recorded with the emission wavelength set at 465 nm. Values of $k_B\tau_{BT}/1 - k_T\nu_{BT}$ calculated from these data are given in Table II and are also plotted according to eq 5 in Figure 5.

The slope of the "least-squares" straight line through the points of Figure 3 yields 1.5 kcal/mol for ΔE, and the intercept of the line gives ln $C = -0.6$ or $C = 0.55$.

The straight-line fit of the plot of Figure 5, the good agreement of the 1.5 kcal/mol value for ΔE obtained from the plot with the ~2 kcal/mol estimate from the phosphorescence spectra, and the fact that the spectral shape and decay of the phosphorescence from BT are independent of the wavelength of the exciting light are consistent with a model in which thermal equilibrium obtains between the triplet states of the two chromophores in BT over the temperature range studied. A necessary condition for this is that triplet energy transfer from one chromophore to the other is much faster than the decay rate of that chromophore triplet. That is, triplet transfer from b to t must proceed with a rate $>10^4$ sec^{-1}, whereas the rate of transfer from t to b need only be >1 sec^{-1}. The existing data on triplet energy transfer[9,10] would predict a rate $\gg 10^4$ sec^{-1} for the b-to-t transfer. One would expect the t-to-b transfer rate to be smaller than the b-to-t rate by the factor $e^{-\Delta E/RT}$[10–12] so that the t to b rate is expected to be $\gg 1$ sec^{-1} over the temperature range.

We do not know what to expect for C, the preexponential factor, except that it should reflect the ratio of densities of the b and t states in the region of crossover, which should be on the order of unity.

The phosphorescence from the benzophenone moiety in BT decays with a rate of approximately ($Ce^{-\Delta E/RT}$)·k_B, that is delayed by the Boltzman factor from the rate of decay of the isolated chromophore. Thus this represents an example of thermally activated delayed phosphorescence. This phenomenon could be called E-type delayed phosphorescence, because it involves a mechanism similar to that for E-type delayed fluorescence[13] in that a higher lying short-lived excited state is populated after thermal activation of a much longer lived lower lying state. However, there are differences between the BT system and the E-type delayed fluorescence exemplified by eosin[13] and fluorescein.[13,14] The delayed fluorescence from the latter compounds is due to thermal repopulation of the fluorescent state from the triplet state, an intrachromophore process which involves an intersystem crossing. The two states do not come to thermal equilibrium, and the C factor is expressed to be $\ll 1$.

We are examining some phenyl ketones which have lowest lying $^3\pi,\pi^*$ states with nearby ^{3}n,π^* states, in order to find an intrachromophore example of the phenomenon reported here. The room-temperature photoreductions of phenylketones possessing lowest lying $^3\pi,\pi^*$ states may involve thermal population of fast-reacting ^{3}n,π^* states.[15–17] The temperature dependence of the fluorescent emissions from azaaromatics should be carefully examined to test for the possibility that in some of these compounds the emitting $^1\pi,\pi^*$ state is not the lowest lying excited singlet state, but that there is a lower lying ^{1}n,π^* state.[18]

Acknowledgments. The author thanks F. H. Doleiden for his capable technical assistance and J. Eisinger for the use of his spectrometer.

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(10) See A. A. Lamola, *Tech. Org. Chem.*, **14**, 17 (1969).

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(18) NOTE ADDED IN PROOF. The decrease in k_B at temperatures above 166°K is probably due to E-type delayed fluorescence in B: J. Saltiel, *et al.*, *ibid.*, **92**, 410 (1970). The emission spectrum of B in poly(methyl methacrylate) is too broad to allow resolution of the phosphorescence and delayed fluorescence.