pseudo-first-order rate constant per hydrogen of 1.9 × 10^{-5} $\sec^{-1}$ at 120.4°; ring exchange required much higher temperatures. The ^{13}C spectrum of deuterated **8** obtained after 185 hr at 185° revealed extensive exchange at the ortho (C-3,8) and para (C-5,6) positions. The isotope-shifted components of the meta (C-4,7) signal showed zero, one, and two deuterium atoms on geminal carbons. The relative exchange rates at 204° (see **8**) may be compared with those for toluene[10,11] shown in **9**; although toluene exchange has been interpreted in terms of phenyl anions, the preferential ortho/para exchange in **8** suggests a different mechanism.

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D. H. Hunter, A. L. Johnson, J. B. Stothers*
Department of Chemistry
University of Western Ontario, London, Canada

A. Nickon, J. L. Lambert, D. F. Covey
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

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A Direct Method for Determining Light Intensity Dependent Rates. Triplet–Triplet Annihilation in Benzophenone

Sir:

We wish to report a novel technique for the evaluation of triplet–triplet annihilation rate constants based on the interrogation of either the integrated phosphorescence emission, or integrated absorption decay, monitored 180° from the axis of excitation. This technique avoids the necessity of making corrections for variations in light intensity along the excitation pathway.[1] The mathematical treatment of the emission or absorption observations is summarized here, and an example of the method is provided.

The decay of the excited triplet state can be expressed by the general equation

$$\mathrm{d}[\mathrm{T}_1]/\mathrm{d}t = -k_1[\mathrm{T}_1] - mk_2[\mathrm{T}_1]^2 \qquad (1)$$

where k_1 is the summation of all radiative and unimolecular and pseudo-unimolecular nonradiative deactivation processes, and k_2 is the overall rate constant for the spin-allowed process

$$\mathrm{T}_1 + \mathrm{T}_1 \xrightarrow{k_2} \mathrm{S}_n + \mathrm{S}_0 \qquad (2)$$

This so-called triplet–triplet annihilation process yields a ground-state singlet, S_0, and one excited state singlet, S_n, with two possible resulting situations as follows.

(a) Internal conversion and intersystem crossing result in very efficient repopulation of the triplet state by $S_n \rightarrow T_1$, as occurs in benzophenone, so that $m = 1$ (eq 1), or (b) chemical reactions, as in biacetyl,[2] and/or other deactivation pathways, dominate with S_n so as to preclude repopulation of T_1 and $m = 2$. In the following derivation, we are assuming condition a holds.

In a pulsed experiment, the density of triplets in an incremental volume about the position x is given by the solution to eq 1 which is

$$n(t,x) = n(0,x)/[e^{k_1 t} + (k_2/k_1)n(0,x)(e^{k_1 t} - 1)] \qquad (3)$$

where $n(0,x)$ is the initial triplet concentration at $t = 0$. Under conditions where the second term in the denominator of eq 3 approaches or exceeds $e^{k_1 t}$, the phosphorescence decay becomes nonexponential. Because of the variation in $n(0, x)$, however, along the excitation path, it is difficult[1] to evaluate k_2 in conventional[3,4] flash-emission and -absorption experiments, and almost prohibitive for situations where the concentration of absorbing species is high.

From Beer's law, the initial triplet concentration with respect to path length, x, along the incident line of excitation through the sample cell is

$$n(0,x) = \alpha I(0,0)e^{-\beta x} \qquad (4)$$

where $I(0,0)$ is the incident intensity of pulsed radiation at $t = 0$ and $x = 0$,[5] β is the optical density of the material being excited, and α is a constant which converts $I(0,0)$ into units of concentration.

The integrated triplet concentration, $n(t,x)$, as a function of time along the path of the penetrating exciting pulse is thus

$$\int_0^l n(t,x)\mathrm{d}x = \{[\alpha I(0,0)e^{-k_1 t}]/\beta\} \times$$

$$\int_0^{\beta l} [e^{-\beta x}\mathrm{d}(\beta x)]/[1 + (k_2/k_1)\alpha I(0,0)(1 - e^{-k_1 t})e^{-\beta x}] \qquad (5)$$

The exponential theory for first-order decay processes follows directly, *i.e.*, when $[k_2\alpha I(0,0)] \ll k_1$

$$n(t) \equiv n(t,x)\mathrm{d}x = [\alpha I(0,0)e^{-k_1 t}(1 - e^{-\beta l})]/\beta \qquad (6)$$

which, for total light absorption, *i.e.*, $e^{-\beta l} \rightarrow 0$, reduces to

$$n(t) = [\alpha I(0,0)e^{-k_1 t}]/\beta \equiv n_e(t) \qquad (7)$$

For the case in which the second-order process is important

$$n(t) = [n_e(t)/c(t)] \ln \{[1 + c(t)]/[1 + c(t)e^{-\beta l}]\} \qquad (8)$$

where $c(t) = (k_2/k_1)[\alpha I(0,0)(1 - e^{-k_1 t})]$. Note that for complete light absorption

$$n(t) = [n_e(t)/c(t)] \ln [1 + c(t)] \qquad (9)$$

The number of photons emitted, n_ν, is obtained as follows.[6]

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[1] (a) F. C. Henriques, Jr., and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **62**, 1038 (1940); (b) W. A. Noyes, Jr., and F. C. Henriques, Jr., *J. Chem. Phys.*, **7**, 767 (1939).

[2] (a) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, *J. Amer. Chem. Soc.*, **94**, 13 (1972); (b) C. C. Badcock, H. W. Sidebottom, J. G. Calvert, B. R. Rabe, and E. K. Damon, *ibid.*, **94**, 19 (1972).

[3] C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968.

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[5] We assume for this analysis that the radiation pulse duration is gaussian and short compared to the duration of the emission. These assumptions simplify our treatment but can easily be generalized for different excitation conditions.

Case a. For a system in which second-order processes are negligible, the rate of decay of the triplet density is

$$\mathrm{d}n/\mathrm{d}t = -k_1 n \tag{10}$$

Thus, the number of photons emitted, n_ν, is

$$n_\nu = k_\mathrm{p} S \int_0^\infty \int_0^l n(t,x)\mathrm{d}t\mathrm{d}x \tag{11}$$

where S is the cross-sectional area of the cell and k_p is the rate constant for radiative decay, *e.g.*, phosphorescence. Further, from eq 7

$$n_\nu = [Sk_\mathrm{p}\alpha I(0,0)]/\beta \int_0^\infty e^{-k_1 t}\mathrm{d}t \tag{12}$$

so that

$$n_\nu = [S\alpha I(0,0)]/\beta\Phi_\mathrm{p} \equiv N_\nu \tag{13}$$

where Φ_p is the quantum yield of phosphorescence, $k_\mathrm{p}(k_1)^{-1}$.

Case b. For a system where the second-order process is important, we have from eq 9, 11, and 13, assuming complete light absorption

$$n_\nu = [Sk_\mathrm{p}\alpha I(0,0)]/[\beta\Delta] \int_0^\infty [e^{-k_1 t}/(1 - e^{-k_1 t})] \times \ln\{1 + \Delta(1 - e^{-k_1 t})\} \tag{14}$$

where $\Delta = (k_2/k_1)\alpha I(0,0)$. Substituting $x = (1 - e^{-k_1 t})$ in eq 14, we find

$$n_\nu = N_\nu \int_0^1 \{[\ln(1 + \Delta x)]/x\}\mathrm{d}x \tag{15}$$

in which the integral is a correction factor for the effects of variation in light intensity.

The integrated intensity of the phosphorescence, I_ν, is given by

$$I_\nu = h\nu(\mathrm{d}n_\nu/\mathrm{d}t) = h\nu Sk_\mathrm{p}n(t) \tag{16}$$

so that

$$I_\nu = \{I_\nu(0)/[\Delta(e^{k_1 t} - 1)]\}\ln\{1 + \Delta(1 - e^{-k_1 t})\} \tag{17}$$

where $I_\nu(0)$ evaluated as $t \to 0$[7] is

$$I_\nu(0) = h\nu Sk_\mathrm{p}\alpha I(0,0)/\beta \tag{18}$$

in units of energy/time. Equation 17 thus can be employed to evaluate k_1 and k_2 in a "head-on" experiment where the emission is monitored 180° to the axis of excitation under conditions in which the excitation source is totally absorbed. It is useful to note that $\alpha I(0,0)$ is dependent on the excitation source by

$$\alpha I(0,0) = [\beta I_\mathrm{a} t_{1/2}]/[Sh\nu N] \tag{19}$$

where I_a is the measured intensity (*e.g.*, by actinometry) of the excitation source in units of energy/time, $t_{1/2}$ is the half-width of the excitation pulse (assuming a Gaussian profile), S is the cross-sectional area of the pulse, $h\nu$ is the energy/quantum, and N is Avogadro's number. For example, the maximum value of $\alpha I(0,0)$ from a 100-kW nitrogen laser (λ = 3371 Å, $2t_{1/2}$ = 6 nsec, no light filtering) is approximately 8.5×10^{-10} β/S einstein/vol.[8]

Case c. For the situation where the exciting light is weakly absorbed, $\beta l \ll 1$, it follows from eq 8, after expanding the exponential in eq 4, that

$$n(t) \approx n_e(t)\{(\beta l)/[1 + c(t)]\} \tag{20}$$

and

$$I_\nu \approx I_\nu(0)(e^{-k_1 t})\{(\beta l)/[1 + \Delta(1 - e^{-k_1 t})]\} \tag{21}$$

Note, when Δ is small, eq 21 reduces to

$$I_\nu \approx \beta l I_\nu(0)\{(1 - \Delta)e^{-k_1 t} + \Delta e^{-2k_1 t}\} \tag{22}$$

The result which is valid at short time intervals following excitation is

$$I_\nu \approx \beta l I_\nu(0)\Delta e^{-2k_1 t} \tag{23}$$

which is a modification of the result given by Parker[3] wherein Δ accounts for the light intensity variation.

An Example of the Method. Triplet–Triplet Annihilation in Benzophenone. The phosphorescence decays (irradiation at 3371 Å with a pulsing N_2 laser, 100 kW, $\tau_{1/2} \sim$ 6 nsec) of degassed 0.5 and 1.0 *M* benzophenone in benzene solution at room temperature were analyzed by a curve matching technique. From eq 17, we define the function f(x) where $x = k_1 t$ so that

$$\mathrm{f}(x) = I_\nu/I_\nu(0) = \{\ln[1 + \Delta(1 - e^x)]\}[\Delta e^x - 1]^{-1} \tag{24}$$

Note that f(x) approaches exponential behavior at large x. An initial value for k_1 was estimated from the experimental decay curves at large t values. The relative phosphorescence intensity was plotted as a function of $k_1 t$. This experimental curve was compared to the function f(x) at large values of x, and the experimental parameter k_1 was adjusted until the limiting slope of the experimental curve matched the limiting slope of f(x). The function f(x) was then matched to the experimental curve over the whole range of x with this value of k_1 by adjusting the parameter Δ.

Figure 1 shows the best fit of the experimental points to the function f(x) by this method for the two phosphorescence decays. The derived values of k_1[9] and Δ appear in Table I. We estimate the uncertainty in k_1 as ±5% and in Δ as ±10%.

Recently, using "side-on" monitoring techniques, Yekta and Turro[10] estimated k_2 for benzophenone in

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(6) More correctly, we are interested in the number of photons viewed by the detector. Since photons are emitted over a solid angle of 4π, the fraction of these intercepted by a detector at 180° will vary for photons originating at different points along the optical path. However, when the distance x between the detector and the emission origin (considered to be the volume element $\Delta x \times \Delta y \times \Delta z$) is much greater than the cross-sectional dimensions of the detector, *i.e.*, Y and Z, the solid angle, Ω, approximates YZ/x^2. Further, for the case where the length of the absorbing region Δx is much less than x, the fractional change in the solid angle $\Delta\Omega/\Omega \approx (2\Delta x)/x$. For example, in our experiment, the shortest distance for X was 15 cm, and we estimate Δx at 99% light absorption to be 0.04 cm, so that the maximum variation in Ω is <0.6%. Thus, under our conditions, the number of photons detected $n_\nu(\Omega/4\pi) \approx n_\nu\kappa$ where κ is an experimental constant.

(7) It can be shown that $I_\nu(0)$ is the same for cases a, b, and c.

(8) It is interesting to observe that with this value of $\alpha I(0,0)$, for a system with a high o.d. (*ca.* 10 cm^{-1}), with S = 0.1 cm^2, where k_2/k_1 = $10^6 M^{-1}$, Δ = 8.5. Values of this magnitude were obtained in the benzophenone study and indicate the significance of the light intensity effect on the triplet decay.

(9) The k_1 values are not expected to be the same for the two concentrations because of a self-quenching process

$$^3\mathrm{B}^* + \mathrm{B} \xrightarrow{k_\mathrm{B}} 2\mathrm{B}$$

In the concentration range 0.01–0.25 *M* in benzene solution, the phosphorescence lifetimes and yields show the expected linear dependence on [B] and provide $k_\mathrm{B} = 4.4 \pm 0.1 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$: R. E. Brown, unpublished results.

(10) A. Yekta and N. J. Turro, *Mol. Photochem.*, **3**, 307 (1972).

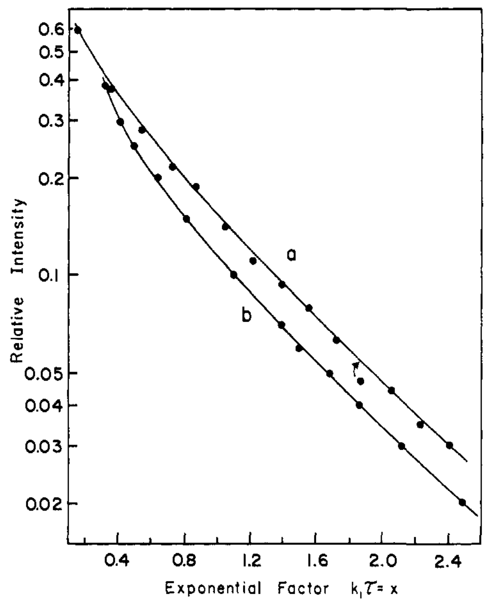

Figure 1. Best fit of data points to function (solid line) f(x): curve a, 1.0 M benzophenone, $k_1 = 3.34 \times 10^5$ sec^{-1}, $\Delta = 6.0$; curve b, 0.5 M benzophenone, $k_1 = 2.40 \times 10^5$ sec^{-1}, $\Delta = 5.0$.

Table I. Derived Deactivation Parameters of the Benzophenone Triplet by the "Head-on" Experiment

[Benzophenone], M	k_1, sec^{-1}	Δ	O.d., cm^{-1}	I(0,0),[a] einstein/(cm^2 pulse)	k_2, M^{-1} sec^{-1}
0.5	2.40×10^5	5.0	60	2.24×10^{-6} [a]	0.89×10^{10} (1.06×10^{10})[b]
1.0	3.34×10^5	6.0	120	2.24×10^{-6} [a]	0.74×10^{10} (1.10×10^{10})[b]

[a] Determined by ferrioxalate actinometry. [b] Corrected for viscosity. The viscosities of the benzophenone solutions relative to pure benzene are 0.5 M, 1.19:1; 1.0 M, 1.48:1.

Freon at room temperature to be $19 \pm 7 \times 10^9$ M^{-1} sec^{-1}. Calvert and coworkers[2b] determined k_2 for biacetyl vapor at 25° using a curve matching procedure that took into account the nonuniformity in the cross-section of the exciting laser pulse.

Further studies are in progress in our laboratory on triplet–triplet annihilation using the "head-on" monitoring and curve simulation procedures.

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Ronald E. Brown, Lawrence A. Singer*[11]
Department of Chemistry, University of Southern California
Los Angeles, California 90007

Joel H. Parks
Department of Physics and Electrical Engineering
University of Southern California
Los Angeles, California 90007

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Proton Coupling Constants in Methylcyclopentadienes

Sir:

Until very recently, the study of the fluxional behavior of metal cyclopentadienyls also containing methyl groups in the ring was rather qualitative. The results of all studies in this field[1] show that the main difficulty is the absence of an adequate method for analyzing the complex pmr spectra.[2] Methylcyclopentadiene ($CH_3C_5H_5$) can be considered as the simplest and most unique model for receiving all information concerning the following questions: how does a methyl group affect the ring proton chemical shifts and how do methyl protons couple with the ring protons?

Methylcyclopentadiene is also a classical model for a study of hydrogen migration. Under equilibrated conditions it consists of a mixture of all three isomers (A_1 or 5, A_2 or 1, and A_3 or 2 isomers; see Table I).

Based on ir,[3] uv,[4] and pmr[5] data, it has been shown that vinylic (A_2,A_3) isomers predominate in the equilibrium at ambient temperatures while the ratio of A_2 and A_3 isomers is close to 1:1 (see data in ref 3–5). Isomer A_1 is thermodynamically unstable and its content does not exceed a few per cent (*ca.* 3%, see ref 3).

Only a qualitative analysis of the pmr spectra of methylcyclopentadiene ($CH_3C_5H_5$) had been performed previously.[5] The difficulties which hindered the complete analysis were due to the fact that: (i) separation of isomers from the mixture is a very laborious task to perform, (ii) slow isomer interconversion takes place due to prototropic rearrangement, (iii) the analysis of the simplest cyclopentadienyl derivatives (including cyclopentadiene itself) has become possible only recently.[6]

We now report the results of complete analysis of the 100-MHz proton magnetic resonance spectra of the equilibrated mixture of methylcyclopentadienes obtained by the distillation of a commercial methylcyclopentadiene. The spectra were obtained on a Varian HA-100 spectrometer for neat liquid; chemical shifts are given in δ scale from internal TMS. The sample was degassed by the usual procedure, and the tubes were sealed before recording the spectra.

The analysis of the pmr spectra of both the vinylic isomers has been performed directly for the mixture using a YaMR-1 simulating program[7] and the indor technique. The indor response has been analyzed with a special INDOR program which finds the true relative signs version starting from the results of the indor experiment. The employment of the indor program is necessary because the spectra include *all possible proton couplings* for isomers A_2 and A_3 (ten constants for each isomer), and we have to choose one of the 2^9 possible sign versions.[8]

(1) See, *e.g.*, (a) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **1**, 323 (1964) (tin); (b) A. Davison and P. E. Rakita, *J. Amer. Chem. Soc.*, **90**, 4479 (1968) (silicon); (c) A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 313 (1970) (silicon, germanium, tin); (d) C. H. Campbell and M. L. H. Green, *J. Chem. Soc, A*, 1318 (1970) (ruthenium); (e) B. Floris, G. Illuminati, and G. Ortaggi, *J. Chem. Soc. D*, 492, (1969); C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, 3282 (1971) (mercury); (f) H. P. Fritz and K. E. Schwarzhans, *Chem. Ber.*, **97**, 1390 (1964) (lead and tin, both two and four coordinated).

(2) Carbon-13 magnetic resonance has been demonstrated to be much more promising in this respect (see Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, *Org. Magn. Resonance*, **4**, 377 (1972)). However, it is limited in sensitivity.

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(8) The INDOR program has been written by M. I. Mstislavsky of this laboratory. The full procedure to analyze the pmr spectra of $CH_3C_5H_5$, as well as $(CH_3)_2C_5H_4$, will be given elsewhere.