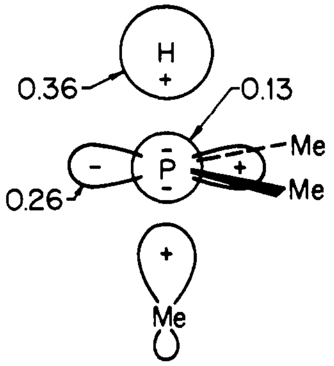


Figure 2. Molecular orbital occupied by the unpaired electron in the trimethylphosphoranyl radical. The values of the spin densities in the contributing atomic orbitals were calculated from the ESR data.

Therefore it appears that the destabilization incurred by the alkyl substitution of the alkoxy group in $Me_2PH(OR)$ is manifested directly by a transfer of spin density from the phosphorus 3s orbital to the σ orbitals of the apical ligands. This is consistent with the antibonding character of the half-occupied three-center orbital in these radicals[3] and fully accords with our earlier expectations. Incidentally, these results must cast further doubt on the purported spectrum[7] of the PH_4 radical. Also, they reveal no indication of a marked change in the geometry of phosphoranyl radicals as the apical ligands become less electronegative.

In conclusion, it seems worthwhile to point out a simple implication of the three-center orbital description for the reactivity of phosphoranyl radicals.[14] It is natural to expect that as a greater spin density moves out from the phosphorus onto the apical ligands, so the lability of organophosphoranyl radicals to α scission should be increased. Since monoalkoxytrialkylphosphoranyl radicals undergo α scission quite readily with the loss of an alkyl radical,[6] this tendency should be even more pronounced for tetraalkylphosphoranyl radicals and might explain the difficulty of alkyl radical addition to trialkylphosphines[6] as compared with trialkyl phosphites.[15]

References and Notes

(1) (a) This work was supported by the U.S. Atomic Energy Commission (Document No. ORO-2968-91); (b) the subject matter of this paper was originally submitted as a communication (December 23, 1974).
(2) For a review, see W. G. Bentrude in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 22, p 595.
(3) T. Gillbro and F. Williams, *J. Am. Chem. Soc.*, **96**, 5032 (1974), and references therein.
(4) A. Hudson and J. T. Wiffen, *Chem. Phys. Lett.*, **29**, 113 (1974).
(5) For a theoretical analysis of the stabilizing influence of electronegative ligands in the apical sites of pentacoordinate phosphorus compounds, see R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972), and references therein.
(6) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 6033 (1972).
(7) C. A. McDowell, K. A. R. Mitchell, and P. Raghunathan, *J. Chem. Phys.*, **57**, 1699 (1972). Note Added in Proof. Since this paper was submitted, the isotropic ESR spectrum of PH_4 in a neopentane matrix has been reported by A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, **62**, 2004 (1975). A similar spectrum was also obtained in a xenon matrix by K. Sogabe, *J. Sci. Hiroshima Univ., Ser. A*, in press, and these results invalidate the earlier work.[7] The isotropic ^{31}P and (apical) ^{1}H hyperfine couplings for authentic PH_4 provide strong support for the conclusions reached in this paper and in ref 3. For a related discussion, see A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Phys. Chem.*, **79**, 651 (1975). We thank Dr. A. Hasegawa for bringing K. Sogabe's work to our attention.
(8) D. Griller and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1339 (1973).
(9) I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 2509 (1973).
(10) T. Dahlgren, T. Gillbro, G. Nilsson, and A. Lund, *J. Phys. E.*, **4**, 61 (1971).
(11) T. Gillbro, C. M. L. Kerr, and F. Williams, *Mol. Phys.*, **23**, 1225 (1974).
(12) For previous examples of ESR spectra showing resolution enhancement but positional invariance of anisotropic spectral features, see C. M. L. Kerr and F. Williams, *J. Am. Chem. Soc.*, **94**, 5212 (1972).
(13) B. Bleaney, *Philos. Mag.*, **42**, 441 (1951).
(14) It has also been suggested in a recent paper (H.-W. Tan and W. G. Bentrude, *J. Am. Chem. Soc.*, **96**, 5950 (1974)) quoting a private communication from J. C. Martin that the three-center bond description with the unpaired electron in the apical positions may provide a better representation of phosphoranyl radicals than the traditional valence-bond picture.
(15) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 2224 (1972).

Singlet Acetone Efficiency and Importance of Triplet Acetone Induced Decomposition of Tetramethyl-1,2-dioxetane from Direct Chemiluminescence[1]

Waldemar Adam,* Nelson Duran,[2] and George A. Simpson[3]

Contribution from the Department of Chemistry and Puerto Rico Nuclear Center, University of Puerto Rico, Rio Piedras, Puerto Rico 00931. Received February 18, 1975

Abstract: From absolute emission intensities and decay lifetimes of the direct chemiluminescent decomposition of tetramethyl-1,2-dioxetane it was established that the singlet excited acetone yields (α) are 0.091 ± 0.033 and 0.05 ± 0.01% at 72 and 22°, respectively. The activation energy for tetramethyl-1,2-dioxetane thermolysis was 25 ± 2 kcal/mol, but the singlet yield (α) was independent of temperature. The induced decomposition efficiency (δ) of the 1,2-dioxetane by triplet acetone was found to be unity in the presence or absence of molecular oxygen, indicating that δ is independent of the lifetime of the triplet acetone sensitizer. The results for the direct chemiluminescent decomposition of tetramethyl-1,2-dioxetane implicate a mechanism in which sensitizing acetone triplets are efficiently replenished.

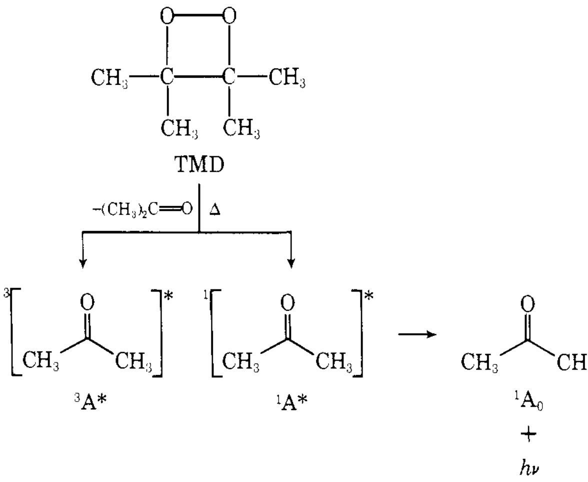
It has been demonstrated that the four-membered ring cyclic peroxide tetramethyl-1,2-dioxetane (TMD)[4] exhibits chemiluminescence on thermal decomposition. Consequently, this "high energy" molecule serves as the chemical energizer of electronically excited singlet and triplet acetone (eq 1). The salient features of this unusual process for TMD follow. Since some 25 kcal/mol activation energy is available: (i) enough chemical energy is stored in TMD to excite

Table I. Decay Lifetimes (τ) and Initial Emission Intensities (I_0) of the Direct Chemiluminescence in the Thermolysis of Tetramethyl-1,2-dioxetane (TMD) in Benzene at 72° [a]

Entry	10^2[TMD], M	τ, min^{-1}	$10^{10}I_0$, einstein/(l. min)	$10^{10}I_0$/[TMD]$_0$, einstein/(mol min)
1	60	19		
2	48	17	143	296
3	40	24		
4	25	27		
5	12	29	28	230
6	2.2	31	9.7	439
7	1.2	29	3.1	332
8	0.44	32	1.9	434
9	0.39	39	1.7	434
10	0.16	39	0.56	352
11	0.062	31	0.17	270
12	0.025	30	0.051	204
13	0.005	30	0.019	386
14[b]	0.005	30	0.019	386
		Av[c] 32 ± 3		Av 337 ± 87
15	0.9		0.0041	0.46
16	1.0	14,300	0.0040	0.42
17	1.0	13,900	0.0042	0.42
		Av 14,100 ± 200		Av 0.43 ± 0.03

[a] Except for the last three entries which were carried out at 22°. [b] Under argon, otherwise atmospheric conditions. [c] For [TMD] less than 0.022 M.

one of the acetone molecules in the triplet or singlet state;[5] (ii) the singlet efficiency is low,[6,7] approximately 0.1-1.0%; (iii) the triplet efficiency is high,[6-8] approximately 50%; (iv) the efficiency of excited state production is temperature independent;[9] (v) triplets induce the decomposition of TMD at high concentrations, especially under deaerated conditions.[10] Related 1,2-dioxetanes displaying these mechanistic traits have been documented.[11-13]



(1)

Recently we have employed a convenient method for determining the number of singlet excited states generated in the thermal decarboxylation of α-peroxylactones by determining the initial emission intensities (I_0) and decay lifetimes (τ) of the direct chemiluminescence.[14] The purpose of the present study was to utilize this method for the TMD decomposition in the hope of determining more precisely the efficiency of chemienergization of excited acetone singlets and assess the importance of the induced decomposition reaction of TMD by triplet acetone in the presence of molecular oxygen.

Experimental Section

TMD was prepared in 16% yield, mp 78-79°,[15] according to the procedure of Kopecky and Mumford.[16] Stock solutions of TMD in benzene were employed.

The method and the photometric apparatus used herein have been described previously.[14] The relative photomultiplier response to acetone fluorescence was within 2% of that of POPOP, which was used as calibration standard. The chemiluminescence emissions were initially recorded in units of volts (V) and converted to emission intensities by the experimentally established conversion factor 5.1 ± 0.5 × 10^{-10} einstein/(V. l. min).

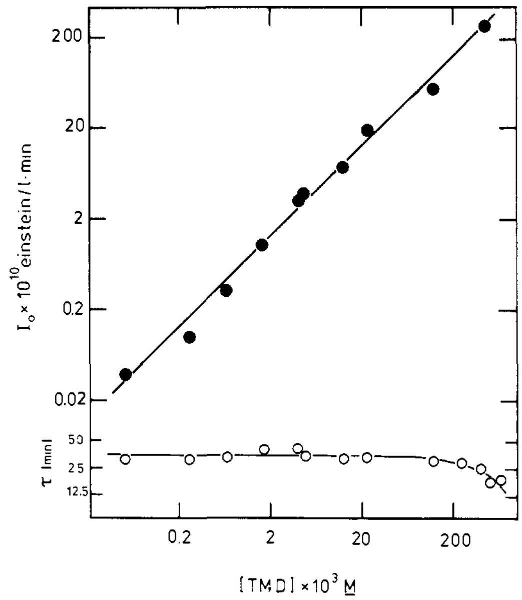


Figure 1. Initial chemiluminescence intensities (I_0) and first-order decay constants (τ) as a function of tetramethyl-1,2-dioxetane concentration.

Constant temperature in the photometer cell compartment was maintained within ±0.5° of the desired temperature by means of a "Colora" constant temperature circulating bath. The cell temperature was periodically monitored with the help of a thermocouple.

Results

The initial emission intensities (I_0) and the decay lifetimes (τ) as a function of [TMD] are collected in Table I and displayed in Figure 1. The I_0 values, i.e. the emission intensities extrapolated to zero reaction time, were the same whether the solvent was preheated to the desired temperature prior to dilution of the TMD stock solution or whether a diluted TMD stock solution was heated from room temperature to the desired reaction temperature directly in the photometer reaction cell. Thus, the loss of sample during the thermal equilibration period (ca. 6 min) was negligible.

The intensity data at 72° (cf. entries 1–14 in Table I) show that the I_0 values are a linear function of [TMD] within a standard deviation of ±26% for the range $10^{-5} \leq [\mathrm{TMD}] \leq 1$ *M*. For example, the $I_0/[\mathrm{TMD}]$ ratio is $[337 \pm 87] \times 10^{-10}$ einstein/(mol min) (cf. last column of Table I). This linear dependence is more dramatically visualized in the log I_0 vs. log [TMD] plot in Figure 1. At low [TMD] the presence or absence of oxygen has a negligible effect on the I_0 values (cf. entries 13 and 14 in Table I). The intensity data at 22° (cf. entries 15–17 in Table I) reveal that the I_0 values are approximately a 1000-fold lower than at 72°, i.e., $0.43 \pm 0.03 \times 10^{-10}$ einstein/(mol min).

The decay lifetimes, defined as $\tau = 1/k$,[14] were determined from semilogarithmic intensity vs. time plots that were recorded continuously for the chemiluminescent TMD decomposition, following first-order kinetics out to about three half-lives. The τ values at 72° (cf. entries 1–15 in Table I) are constant for [TMD] < 0.1 *M*, i.e., $\tau_{\mathrm{av}} = 32 \pm 3$ min. For [TMD] > 0.1 *M* the values are a function of [TMD], following the empirical relation given in eq 2. The parameters 0.00 and 1.28 *M* were obtained by a least-square fitting of the experimental data, using a $[32/\tau - 1]^{-1}$ vs. $[\mathrm{TMD}]^{-1}$ plot for [TMD] > 0.1 *M*. Again, the τ values were insensitive to the presence or absence of oxygen (cf. entries 13 and 14 in Table I) at low [TMD]. However, the few data points at 22° show that the τ values are ca. 500-fold larger than at 72° (cf. the respective τ_{av} values in Table I). An approximate activation energy $E_a = 25 \pm 2$ kcal/mol was extrapolated from these limited data.

$$k = 1/\tau = 0.031 \left\{1 + \left[0.00 + \frac{1.28\ M}{[\mathrm{TMD}]}\right]^{-1}\right\} \mathrm{min}^{-1} \qquad (2)$$

Previously[14] we defined the direct chemiluminescence quantum yield (Φ_{DC}) according to eq 3. Using the data in Table I, we calculate that the Φ_{DC} values are ($11 \pm 4 \times 10^{-7}$ and $6 \pm 1 \times 10^{-7}$ einstein/mol at 72 and 22°, respectively. Thus, within the experimental error the direct chemiluminescence efficiencies are temperature independent.

$$\Phi_{\mathrm{DC}} = (I_0/[\mathrm{TMD}]_0)\tau \qquad (3)$$

Mechanistic Interpretations

The mechanism which rationalizes our data for the TMD chemiluminescence (cf. Table I and Fig. 1) is shown in Scheme I below. The parameters α, β, γ, and δ represent excited singlet acetone (^{1}A*), excited triplet acetone (^{3}A*), ground state singlet acetone ($^1\mathrm{A}_0$), and TMD induced decomposition efficiencies, respectively. In accordance with our data, this mechanism predicts that the time dependence of the emission intensity (I_t) is given by eq 4. In this equation the fluorescence efficiency of acetone is $\phi_{\mathrm{F}} = k_3/(k_2 + k_3 + k_4)$ and k the observed rate constant, which is a complex function of [TMD], as shown in eq 5, in which the total triplet acetone efficiency $\beta' = \beta + \phi_{\mathrm{ISC}}\alpha$ and $\phi_{\mathrm{ISC}} = k_4/(k_2 + k_3 + k_4)$. A similar equation was derived for the α-peroxylactone chemiluminescence[14] and in this derivation it was assumed steady state dependence of ^{3}A* on [TMD] held only for the initial rates at which TMD consumption is minimal.

$$\mathrm{TMD} \xrightarrow{k_1} \alpha\ {}^1\mathrm{A}^* + \beta\,{}^3\mathrm{A}^* + \gamma\,{}^1\mathrm{A}_0$$
$${}^1\mathrm{A}^* \xrightarrow{k_2} {}^1\mathrm{A}_0$$
$${}^1\mathrm{A}^* \xrightarrow{k_3} {}^1\mathrm{A}_0 + h\nu$$
$${}^1\mathrm{A}^* \xrightarrow{k_4} {}^3\mathrm{A}^*$$
$${}^3\mathrm{A}^* \xrightarrow{k_5} {}^1\mathrm{A}_0$$
$${}^3\mathrm{A}^* + \mathrm{TMD} \xrightarrow{k_6} \delta\,{}^3\mathrm{A}^* + (3 - \delta)\,{}^1\mathrm{A}_0$$

$$I_t = \alpha\phi k_1[\mathrm{TMD}]_0 \exp(-kt) \qquad (4)$$

$$k = k_1\left\{1 + \left[\left(\frac{1 - \delta}{\beta'}\right) + \frac{1}{\beta'\tau_5/k_6[\mathrm{TMD}]}\right]^{-1}\right\} \qquad (5)$$

Since in eq 5 the observed rate constant k depends on the efficiency of the induced decomposition (δ) of TMD by ^{3}A* (step k_6), in principle it should be possible to assess the importance of this induced decomposition from our experimental data with the help of eq 5. Furthermore, it should be clear that induced decomposition should be important at high [TMD] because at low [TMD] the complex dependence of k on [TMD] (eq 5) reduces to $\lim_{[\mathrm{TMD}]\to 0} k = k_1$; i.e., the observed rate constant k becomes the unimolecular rate constant k_1 for the first step. Consequently, k_6 enters as the crucial perturbational parameter in the dependence of the observed rate constant k and thus the decay lifetime τ on [TMD] in eq 5.

Our τ data (cf. Figure 1) show that the induced decomposition becomes significant for [TMD] > 0.1 *M*. We have, therefore, a mechanistic rationale for the empirical relationship between τ and [TMD] in eq 2. For example, comparing eq 2 with eq 5, we observe that $k_1 = 0.031\ \mathrm{min}^{-1}$, $(1 - \delta)/\beta' \simeq 0.00$ and $\beta' k_6 \tau_5 = 0.78\ M^{-1}$, where τ_5 is the actual lifetime of acetone triplets under oxygen conditions.

Furthermore, as supported by our data, eq 4 predicts that the initial emission intensity (I_0) depends directly on the initial [TMD], i.e., at t_0 eq 4 reduces to eq 6. Comparing eq 3 and eq 6, we notice that the direct chemiluminescence yield (Φ_{DC}) is the product of the singlet efficiency (α) and fluorescence efficiency of acetone (ϕ_{F}), experimentally evaluated in terms of the $I_0/[\mathrm{TMD}]_0$ and τ values of Table I (eq 7). Since $\phi_{\mathrm{F}} = 1.2 \times 10^{-3}$ for acetone,[14] and assuming the fluorescence yield does not vary appreciably between 22 and 72°, our data afford singlet acetone yields (α) of 0.091 ± 0.033 and 0.05 ± 0.01% at 72 and 22°, respectively. Within the experimental error we conclude that α is independent of temperature.

$$I_0 = \alpha\phi_{\mathrm{F}} k_1[\mathrm{TMD}]_0 \qquad (6)$$

$$\Phi_{\mathrm{DC}} = \alpha\phi_{\mathrm{F}} = (I_0/[\mathrm{TMD}]_0)\tau_1 \qquad (7)$$

Comparison with Previous Results

Our results compare favorably with previously published data on TMD. For example, the range of singlet acetone yields determined by a variety of methods was $0.1\% < \alpha < 1\%$ at 72°. Our value is $\alpha = 0.091 \pm 0.33\%$ and coincides with the lower limit of the established range.[6] In view of the fact that our method entails a direct and absolute chemiluminescence intensity measurement, we feel that the lower limit of $\alpha \simeq 0.1\%$, determined by ferrioxalate actinometry,[6] is the more reliable one.

Our finding that the singlet efficiency (α) is independent of temperature is also in harmony with previous work[9] which established a negligible activation energy for this process. Also our data confirm an activation energy $E_a \sim 25$ kcal/mol for the thermal decomposition of TMD.[17]

More significant, our data stress the importance of the induced decomposition step k_6 (acetone triplets sensitizing the decay of TMD) even in the presence of molecular oxygen when [TMD] > 0.1 *M*. From the dependence of the observed rate constant k on [TMD] (eq 5), we determined that the efficiency of induced decomposition was $\delta \simeq 0.99$ in the presence of oxygen, using the triplet efficiency of $\beta =$

0.5.[6] In the absence of oxygen Turro et al.[10] found also $\delta = 0.98$, but employing a considerably more complex integrated rate expression. Besides the convenience of analyzing the effect of the induced decomposition directly on the observed rate constant k (eq 5), the significant conclusion is that δ is independent of the lifetime of the sensitizer, namely triplet acetone. In other words, irrespective of the presence or absence of the triplet quencher oxygen, every induced decomposition encounter (step k_6) conserves the number of triplet acetone sensitizers by destroying a TMD molecule. Thus, these results imply that the postulated[4,18] TMD·^{3}A* complex is independent of the unquenched or oxygen quenched acetone triplet lifetime.

In degassed solutions it was established that $kq\ \tau_T = 1000\ M^{-1}$ (50% error limit),[10] while in aerated solutions we found $\beta' k_6 \tau_5 = 0.78\ M^{-1}$ (17% error limit) for the TMD decomposition. If it is assumed that this difference is due solely to oxygen quenching effect, a long triplet state lifetime of acetone in benzene solution results. Using $\beta' = 0.5$ (determined by Turro and Lechtken[6]) and $\tau_5 \simeq 10^{-7}$ sec (suggested by Turro et al.[7]), we estimate that the natural lifetime of acetone triplets falls in the range $10^{-4} < \tau_T < 10^{-5}$ sec. This is in accord with acetone triplet lifetimes reported in acetonitrile solution[19] and in the gas phase;[20] however, these values are in serious disagreement with the value of 3×10^{-8} sec extrapolated from benzene quenching data.[21] Resolution of this discrepancy must await further work, either using photophysical measurements or photosensitized reactions of acetone in benzene solution.

In conclusion, the present method of determining the absolute emission intensities and rate constants is direct, simple, and convenient for studying the mechanism of chemiluminescent reactions. Reliable and useful data on singlet efficiencies, induced decomposition efficiencies, activation parameters, and lifetimes of excited states can be acquired by this method. Of particular advantage is the large concentration range dependence (ca. 10^5) that can be assessed for the emission intensities and rate constants, providing a high level of confidence in the mechanistic interpretations. As was illustrated for α-peroxylactone decarboxylations,[14] this method is useful for studying enhanced chemiluminescence intensities, permitting determination of triplet yields (β) Such a study is presently under way for TMD.[22]

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully appreciated. We thank Professor J. W. Hastings for a Mitchell-Hastings photometer, as well as calibrating one of our "POPOP" cocktails.

References and Notes

(1) This is paper XXXVII in the Cyclic Peroxide series. For Paper XXXVI, cf. W. Adam and J. Arce, *J. Am. Chem. Soc.*, **97**, 926 (1975).

(2) On study leave from the Department of Chemistry, Catholic University of Valparaiso, Chile.

(3) Puerto Rico Nuclear Center. This paper was prepared in connection with work under contract No. AT-(40-1)-1833 with the U.S. Atomic Energy Commission.

(4) N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H.-C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974).

(5) P. Lechtken and G. Höhne, *Angew. Chem., Int. Ed. Engl.*, **12**, 772 (1972).

(6) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972).

(7) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H.-C. Steinmetzer, and W. Adam. *J. Am. Chem. Soc.*, **96**, 1627 (1974).

(8) H. C. Steinmetzer, P. Lechtken, and N. J. Turro, *Justus Liebigs Ann. Chem.*, 1984 (1973).

(9) H.-C. Steinmetzer, A. Yekta, and N. J. Turro, *J. Am. Chem. Soc.*, **96**, 282 (1974).

(10) P. Lechtken, A. Yekta, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3027 (1973).

(11) T. Wilson and A. P. Schaap, *J. Am. Chem. Soc.*, **93**, 4126 (1971).

(12) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neal, *J. Am. Chem. Soc.*, **96**, 7525 (1974).

(13) T. R. Darling and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 1625 (1974).

(14) W. Adam, G. A. Simpson, and F. Yany, *J. Phys. Chem.*, **78**, 2559 (1974).

(15) CAUTION! At times TMD explodes violently during attempts to take melting points.

(16) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); private communications.

(17) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **95**, 264 (1973).

(18) N. J. Turro, N. E. Schore, H.-C. Steinmetzer, and A. Yekta, *J. Am. Chem. Soc.*, **96**, 1936 (1974).

(19) G. Porter, R. W. Yip, J. M. Dunnston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, **67**, 3149 (1971).

(20) R. B. Cundall and A. S. Davies, *Prog. React. Kinet.*, **4**, 1 (1967).

(21) R. O. Loutfy and R. W. Yip, *Can. J. Chem.*, **51**, 1881 (1973).

(22) Preliminary results on the enhanced chemiluminescence of TMD in the presence of either 9,10-diphenylanthracene or 9,10-bis(phenylethynyl)anthracene, observed previously to be affected negligibly by triplet energy transfer,[8] gave singlet excited acetone yields an order of magnitude lower than the present value $\alpha \simeq 0.1\%$. The poor agreement between the enhanced and direct yields is attributed to either self-quenching or reabsorption effects at the high enhancer concentrations ($\sim 10^{-2}$ *M*) required for efficient energy transfer.

Photoelectron Spectra of Open Chain C_6H_6 Isomers

Peter Bischof,[1] Rolf Gleiter,*[1] Henning Hopf,[2] and Frank T. Lenich[2]

Contribution from the Institut für Organische Chemie der Technischen Hochschule Darmstadt, D-61 Darmstadt, Germany, and the Institut für Organische Chemie der Universität Karlsruhe, D-75 Karlsruhe, Germany. *Received February 5, 1975*

Abstract: The He I photoelectron spectra of 1,2,4,5-hexatetraene (biallenyl, **1**), 3-methyl-1,2,4,5-hexatetraene (3-methylbiallenyl, **2**), 1,2,4-pentatriene (vinylallene, **3**), 1,2-hexadiene-5-yne (propargylallene, **4**), and 1,5-hexadiyne (bipropargyl, **5**) are presented. The assignments of the photoelectron bands are discussed in terms of ZDO molecular orbital models as well as of semiempirical calculations. It is shown that (i) the first four bands of the photoelectron spectra of **1**, **2**, **4** and **5** and the first three bands of the photoelectron spectra of **3** are due to the ionization out of a π-orbital and (ii) that interaction between the C–C bond connecting the olefinic moieties and the corresponding π-orbitals is important.

The electronic structure of conjugated and cumulated double bonds has been subject to many investigations by experimental as well as theoretical chemists.[3] We would like to add some further information on this theme by reporting the photoelectron (PE) spectra of 1,2,4,5-hexatetraene (biallenyl, **1**), 3-methyl-1,2,4,5-hexatetraene (3-methylbiallyl, **2**), 1,2,4-pentatriene (vinylallene, **3**), 1,2-hexadiene-5-yne (propargylallene, **4**), and 1,5-hexadiyne (bipropargyl, **5**).