J. Am. Chem. Soc. 1983, 105, 714-719

The Azoalkane 7,8-Benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene as Spin State Specific Chemical Titrant of Singlet and Triplet Excitation Generated in the Thermolysis of Dioxetanes

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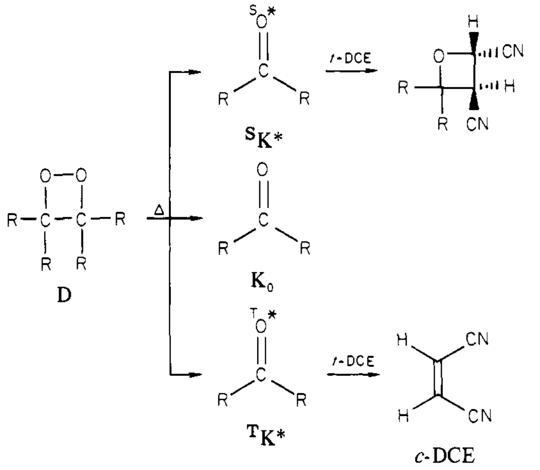
Abstract: A convenient and sensitive analytical method for the chemical titration of chemienergized singlet excited carbonyl products generated in the thermal decomposition of 1,2-dioxetanes is described. This novel method engages the spin state specific photodenitrogenation of the azoalkane 7,8-benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene into 2,3-benzotricyclo-[3.2.0.0^{4,6}]hept-2-ene (BTH) as chemical titrant, using capillary gas chromatography (CGC) in the quantitation of BTH. Provided the singlet energy of the chemienergized carbonyl product is greater than 79 kcal/mol, the present method allows the determination of singlet excitation yields (ϕ^S) as low as 0.05% within an error margin of ca. 15%. Furthermore, it is shown that the triplet spin state specific photorearrangement of the azoalkane BDT into 7,8-benzo-2,3-diazatricyclo[4.3.0.0^{2,9}]nona-3,7-diene might be a potentially useful method for the chemical titration of triplet carbonyl products chemienergized in the thermolysis of 1,2-dioxetanes.

In a now classical experiment Turro and Lechtken[1a] demonstrated elegantly that the singlet and triplet quantum yields of electronically excited acetone, respectively ϕ^S and ϕ^T, in the thermal decomposition of an 1,2-dioxetane (D) can be assessed quantitatively via chemienergized photochemical transformations of 1,2-dicyanoethylene (eq 1). Thus, for the specific case of the trans isomer (t-DCE), the singlet excited ketone ($^SK^*$) gave exclusively the oxetane product via Paterno–Büchi cycloaddition, while the triplet excited ketone ($^TK^*$) led only to the cis isomer (c-DCE) via trans/cis photoisomerization. Originally the important and useful concept of "chemical titration" of excited states, a technique of great analytical value in the determination of chemiexcitation yields, was illustrated by White et al.[1b] The spin state specific nature of the DCE titrant was a particularly useful feature, because it allowed the determination of the ϕ^S and ϕ^T excitation parameters of dioxetanes separately. However, practical limitations have encumbered widespread use of DCE as chemical titrant. For example, the relatively low quantum yields for the photoreactions in eq 1 curtailed the sensitivity of the method, while efficient thermal cis/trans isomerization at elevated temperatures limited the use of relatively stable dioxetanes. Finally, the reversibility of the trans $\rightleftarrows$ cis photoisomerization necessitated low conversions, thereby introducing large errors in the quantitative analysis.



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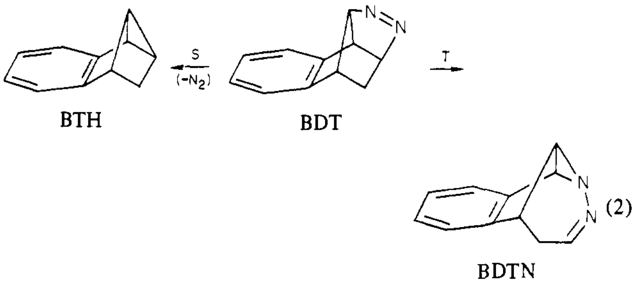
Other chemical titrants were developed and reported to circumvent these menacing practical problems.[2] For example, for the titration of chemiexcited triplet states trans/cis isomerization of stilbene,[3] the cycloaddition with 2-methyl-2-butene[4] and with 2-butyne,[5] or the di-π-methane rearrangement of benzonorbornadiene[6] were employed. None of these methods were effective for the quantitation of the chemienergized singlet states.

Clearly, it seemed important and relevant to search for efficient and effective spin state specific chemical titrants, especially for singlet excited states. A photochemical substrate of potential usefulness for this purpose was the azoalkane 7,8-benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene (BDT), which we recently demonstrated[7] to exhibit spin state specific photoreactions, leading exclusively to 2,3-benzotricyclo[3.2.0.0^{4,6}]hept-2-ene (BTH) under singlet excitation and exclusively to 7,8-benzo-2,3-diazatricyclo-[4.3.0.0^{2,9}]nona-3,7-diene (BDTN) under triplet excitation (eq 2). Herein we report our results on the utilization of the azoalkane BDT as useful chemical titrant of singlet and triplet excited states generated in the thermolysis of dioxetanes.



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† Diplomarbeit, University of Würzburg, June 1981.

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Scheme I

(a) Dioxetane Decomposition:

$$D \xrightarrow{k_0} K_0 + K_0 \tag{3}$$

$$D \xrightarrow{k^S} {}^{S}K^* + K_0 \tag{4}$$

$$D \xrightarrow{k^T} {}^{T}K^* + K_0 \tag{5}$$

(b) Singlet-State Reactions:

$${}^{S}K^* \xrightarrow{k_d^S} K_0 \tag{6}$$

$$BDT + {}^{S}K^* \xrightarrow{k_{et}^{SS}} K_0 + {}^{S}BDT^* \tag{7}$$

$${}^{S}BDT^* \xrightarrow{k_{d'}^S} BDT \tag{8}$$

$${}^{S}BDT^* \xrightarrow{k_r^S} BTH \tag{9}$$

$${}^{S}BDT^* \xrightarrow{k_f} BDT + h\nu_f \tag{10}$$

(c) Triplet-State Reactions:

$${}^{T}K^* \xrightarrow{k_d^T} K_0 \tag{11}$$

$$BDT + {}^{T}K^* \xrightarrow{k_{et}^{TT}} K_0 + {}^{T}BDT^* \tag{12}$$

$${}^{T}BDT^* \xrightarrow{k_{d'}^T} BDT \tag{13}$$

$${}^{T}BDT \xrightarrow{k_r^T} BDTN \tag{14}$$

The elementary chemical steps that are involved in such chemical titration are collected in Scheme I, subdivided into the three processes: (a) dioxetane decomposition, (b) singlet-state reactions, and (c) triplet-state reactions. With the help of steady-state kinetics, it can readily be shown that the quantum yield of BTH formation via singlet chemiexcitation is given by eq 15, where ϕ^S is the singlet excitation yield (eq 4), ϕ_{et}^{SS} is the

$$\phi_{BTH} = \phi^S \phi_{et}^{SS} \phi_r^S \tag{15}$$

quantum yield of singlet–singlet energy transfer (eq 7), and ϕ_r^S is the photochemical efficiency of the BDT → BTH conversion (eq 9). Of these terms ϕ_{BTH}, i.e., the chemical yield of BTH product per unit concentration of dioxetane decomposed, is determined experimentally. If the photochemical efficiency ϕ_r^S is not known under the experimental conditions employed in the chemical titration, one is obliged to determine it by the usual photomechanistic techniques. Thus, once the energy transfer efficiency ϕ_{et}^{SS} is known, the desired singlet quantum yield ϕ^S can be readily evaluated. Since ϕ_{et}^{SS} depends on the concentration of the azoalkane BDT (cf. eq 7), algebraic reorganization of eq 15 leads to eq 16. Thus, a double reciprocal plot of ϕ_{BTH} vs.

$$\frac{1}{\phi_{BTH}} = \frac{1}{\phi^S}\frac{1}{\phi_r^S}\left\{1 + \frac{k_d^S}{k_{et}^{SS}[BDT]}\right\} \tag{16}$$

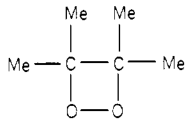
[BDT] gives as intercept eq 17, at infinite BDT concentration the

$$\frac{1}{\phi_{BTH}^{\infty}} = \frac{1}{\phi^S}\frac{1}{\phi_r^S} \text{ or } \phi^S = \phi_{BTH}^{\infty}/\phi_r^S \tag{17}$$

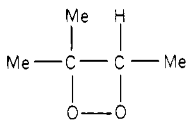
energy transfer efficiency ϕ_{et}^{SS} of eq 7 is unity. If ϕ_{BTH}^{∞} and ϕ_r^S are known, the singlet excitation yield ϕ^S can be assessed in this singlet-state titration. Quite analogously, for the triplet-state titration eq 18 can be derived from the respective elementary steps

$$\phi^T = \phi_{BDTN}^{\infty}/\phi_r^T \tag{18}$$

in Scheme I. Equation 18 permits us to evaluate the triplet excitation yield ϕ^T by determining experimentally the quantum yield of BDTN product formation at infinite BDT concentration and the photochemical yield of the BDT → BDTN rearrangement under the conditions of the dioxetane thermolysis. With the help of these equations we will now proceed to apply the spin state specific chemical titration techniques to determine the excitation parameters ϕ^S and ϕ^T of the dioxetanes **1a–e** and compare our results with reported data.



1a



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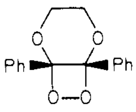

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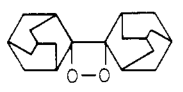

1d

1e

Results and Discussion

Excitation Energies of the Azoalkane BDT. For energy transfer from the chemienergized excited ketone to the azoalkane titrant BDT to be efficient, the excitation energy of BDT should be lower than that of the excited ketone. It was, therefore, important to assess the singlet (E_S) and triplet (E_T) excitation energies of BDT. Thus, to estimate E_S, we measured the absorption (λ_{max} = 354 nm) and fluorescence (λ_{max} = 377 nm) spectra and the half-distance between the respective maxima taken, affording $E_S \sim$ 78.5 kcal/mol in benzene.

In the absence of efficient phosphorescence, the triplet excitation energy had to be determined by bracketing, using a variety of triplet sensitizers, e.g., acetone (80), benzophenone (68.6), 9,10-anthraquinone (62.4), phenanthrene (61.9), naphthalene (60.9), 2,3-butadione (56.3), and benzil (53.4), for which their triplet energies in kcal mol^{-1} are given in parentheses. Triplet sensitization of the spin state specific BDT → BDTN rearrangement could be achieved down to 9,10-anthraquinone, establishing herewith that 61.9 kcal/mol < E_T < 62.4 kcal/mol. Therefore, the azoalkane BDT should be a potentially useful chemical titrant of dioxetanes that chemienergize excited ketones with $E_S \geq 79$ kcal/mol and $E_t \geq 62$ kcal/mol, provided the photochemical quantum yields ϕ_r^S and ϕ_r^T are large enough to enable detection of the chemienergized photoproducts of BDT.

Photochemical Quantum Yields of Azoalkane BDT. As eq 17 and 18 show, the photochemical quantum yields ϕ_r^S for the singlet-state reaction BDT → BTH and ϕ_r^T for the triplet state reaction BDT → BDTN are necessary in order to assess the ϕ^S and ϕ^T excitation parameters of a dioxetane. Since these were not known for these photochemical reactions[7] of the azoalkane BDT, we were obliged to determine them at the conditions of the dioxetane thermolysis conditions.

For the singlet state specific denitrogenation of azoalkane BDT into the benzotricycloheptene BTH, direct irradiation at 342 nm was carried out to evaluate ϕ_r^S. For calibration of the light flux, the well-known ferrioxalate actinometer[8] was used, as well as the denitrogenation of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), for which the quantum yield of nitrogen loss is known[9] to be 100%. The actinometry was monitored by UV spectrophotometry.

As the results in Table I reveal, the denitrogenation efficiency is temperature dependent. The analytical technique that was

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Table I. Temperature Dependence of the Photochemical Quantum Yield (ϕ_r^S) and Fluorescence Quantum Yield (ϕ_f) of 7,8-Benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene (BDT)[a]

							E_a, kcal/mol
temp,[b] °C	21.0	22.5	39.5	49.5	60.5	75.0	3.4 ± 1
ϕ_r^S,[c] %	51	53	60	65	66	75	
temp,[b] °C	24.0	39.0	58.5	72.4			3.8 ± 1
ϕ_f,[d] %	8.7	6.6	4.6	3.7			

[a] 0.02 M solutions in benzene for ϕ_r^S, and 8.3×10^{-5} M in benzene for ϕ_f; control experiment showed that ϕ_r^S and ϕ_f are independent of DBT concentration. [b] Temperature control within ±1 °C. [c] By determination of the chemical yield of BTH with capillary gas chromatography on a 50-m OV 101 capillary column, operated at 130 °C and a N_2 carrier gas flow of 1.1 mL/min; photolyses were run by irradiation at 342 nm. [d] Run on a Perkin-Elmer Model MPF-44B spectrofluorimeter by excitation at 340 nm; relative uncorrected values. 9,10-Diphenylanthracene was used as standard ($\phi_f^{DPA} = 0.83$).

employed to assess the temperature coefficient of the ϕ_r^S quantum yield consisted of determining the chemical yield of BTH by capillary gas chromatography (CGC) as a function of temperature. Since $\phi_r^S = k_r^S/(k_r^S + k_f + k_{d'}^S)$ and $k_r^S = A \exp(-E_a/RT)$, the Arrhenius activation energy (E_a) for the denitrogenation of BDT could be readily computed with the help of eq 19. Thus, an

$$\ln [\phi_r^S/(1 - \phi_r^S)] = \ln [A/(k_f + k_{d'}^S)] - E_a/RT \qquad (19)$$

Arrhenius plot of $\ln [\phi_r^S/(1 - \phi_r^S)]$ vs. $1/T$ gave as slope E_a = 3.4 ± 1 kcal/mol.

Alternatively, this activation energy could be determined by means of the temperature dependence of the fluorescence quantum yield ϕ_f of the azoalkane BDT[10] (eq 10), providing an internal check of our data. The published methods were employed for this purpose.[11] Again, with the definitions $\phi_f = k_f/(k_f + k_{d'}^S + k_r^S)$ and $k_r^S = A \exp(-E_a/RT)$, the temperature dependence of k_r^S is given by eq 20, assuming that k_f is temperature independent

$$\ln (\phi_f^{-1} - 1) = -E_a/RT + \ln (A/k_f) \qquad (20)$$

and $k_r \gg k_{d'}$. An Arrhenius plot of $\ln (\phi_f^{-1} - 1)$ vs. $1/T$ gives a slope E_a = 3.8 ± 1.0 kcal/mol. Indeed, within experimental error the activation energies for denitrogenation of BDT determined from the temperature dependence of ϕ_r^S and ϕ_f match satisfactorily. Also the absolute value of ca. 4 kcal/mol agrees well with published data for other azoalkane denitrogenations.[12]

Quite analogously the photochemical yield of the triplet state specific rearrangement of azoalkane BDT into the aziridine BDTN (eq 14) was determined by means of acetophenone sensitization at 292 nm. This choice of sensitizer and wavelength was dictated by the necessity of minimizing direct irradiation of the azoalkane BDT. For the calibration of the photon flux, the ferrioxalate actinometer[8] was employed. The chemical yield of aziridine BDTN was quantitated by means of HPLC, using a μ-Bondapak C_{18} reversed-phase column and 40:60 methanol/aqueous 0.01 M phosphate buffer as eluant. From the experimental data (Table II), a double reciprocal plot of ϕ_r^T vs. [BDT] gave ϕ_r^T = 64 ± 10% as the intercept. No temperature dependence of ϕ_r^T could be discerned since within experimental error the same values were obtained at 20 and 80 °C.

Table II. Photochemical Quantum Yield (ϕ_r^T) of 7,8-Benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene (BDT)[a]

						ϕ_r^T
run 1	temp,[b] °C	80	80	20	80	
	[BDT], M	0.044	0.110	0.198	0.220	60 ± 10
	ϕ_r^T,[c] %	54.5	57.9	56.9	58.7	
run 2	temp,[b] °C	80	20	80	80	
	[BDT], M	0.020	0.058	0.058	0.156	68 ± 10
	ϕ_r^T,[c] %	60.4	67.6	64.8	67.6	

[a] 0.1 M Acetophenone in benzene as sensitizer, irradiated at 292 nm. [b] Temperature control within ±1 °C. [c] Chemical yield of BDTN (R_f = 245 s) determined by HPLC on a Waters instrument with a μ-Bondapak C_{18} reversed-phase column and 40:60 methanol/0.01 M aqueous phosphate buffer (pH 7.7) as eluant (flow rate 1.7 mL/min at 2500 psi); UV detection at 254 nm; *p*-aminoacetophenone as internal standard (R_f = 155 s).

Table III. Chemical Titration of Excited Singlet-State Acetone with 7,8-Benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene (BDT) in the Thermolysis of Tetramethyl-1,2-dioxetane (TMD)[a]

[BDT], M	0.661	0.472	0.283	0.236	0.189	0.129	0.090
$10^4\phi_{BTH}$[b]	*c*	1.49	2.87	3.64	4.25	14.8	17.4
[BDT], M	0.0644	0.0375	0.0131	0.0094	0.0075	0.0056	
$10^4\phi_{BTH}$[b]	17.3	15.3	9.36	7.85	6.60	5.39	

[a] [TMD] = 0.11 M in benzene heated at 80 °C for 1.5 h. [b] Benzotricycloheptene was quantitated by CGC using a 50-m OV101 column, operated at 130 °C oven temperature and a N_2 carrier gas flow rate of 1.1 mL/min; 2-methylnaphthalene was used as calibration standard of the peak areas. [c] Too low [BTH] for detection.

Singlet Excitation Yields of 1,2-Dioxetanes. With the photochemical quantum yield ϕ_r^S on hand, what remained to be determined was the chemiexcitation quantum yield of benzotricycloheptene (BTH) formation for the dioxetanes **1a**–**e** in order to evaluate their singlet excitation yields according to eq 15. The tetramethyl-1,2-dioxetane (**1a**) (TMD) was employed as test system since abundant data on its excitation yields have been reported.[2]

A preliminary experiment confirmed that indeed the nitrogen extrusion product benzotricycloheptane BTH is formed when a benzene solution of the azoalkane BDT and TMD was heated at 80 °C for 1.5 h (complete consumption of TMD). However, capillary gas chromatography (CGC) was absolutely essential for the detection and quantitation of the small amounts of BTH that were formed in this chemienergized process.

The results of the quantitative analysis of BTH formation in the reaction of BDT and TMD are collected in Table III and displayed in Figure 1. A most peculiar double reciprocal plot of ϕ_{BTH} vs. [BDT] is observed. In the low concentration range, i.e., 0.005–0.05 M BDT, the expected characteristic behavior that the chemical yield ϕ_{BTH} increases with increasing [BDT] is obtained; in fact, the double reciprocal plot is perfectly linear in this region. However, unexpectedly in the high concentration range, i.e., 0.05–0.5 M [BDT], the chemical yield ϕ_{BTH} decreases with increasing [BDT]. The turning point in these two counteracting trends occurs at [BDT] ~ 0.05 M. Control experiments suggest that the mechanistic origin of this peculiar dependence of the double reciprocal plot (Figure 1) in the high [BDT] range is due to a *catalytic* "dark" reaction between the dioxetane and azoalkane.[13]

The low concentration dependence enables an evaluation of the ϕ^S excitation parameters for the dioxetanes under investigation. For example, for our model 1,2-dioxetane, namely TMD, the intercept of the double reciprocal plot (Figure 1) in the low [BDT] range affords ϕ_{BTH}^{∞} = 0.25 ± 0.02% (Table IV) in benzene at 80 °C. Since the photochemical yield for the singlet state specific BDT → BTH denitrogenation is ϕ_r^S = 75 ± 10% (extrapolated from Table I at 80 °C) under these conditions, from eq 17 we calculate that the excitation yield of singlet excited acetone is ϕ^S = 0.31 ± 0.04%. This is in good agreement with the reported data, which range from 0.04 to 0.4%, but cluster mainly around 0.25 ± 0.14%.[2]

From the double reciprocal plot of ϕ_{BTH} and [BDT] also the rate constant k_{et}^{SS} of the energy transfer between excited singlet acetone from TMD to the azoalkane BDT (eq 7) can be estimated. The quotient of the intercept and slope of such a double reciprocal

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[10] The absolute fluorescence quantum yield of BDT was determined relative to 9,10-diphenylanthracene as standard, affording ϕ_f = 0.05 in cyclohexane at 25 °C with a singlet lifetime τ_S ~ 0.7 ns (Prof. K. Sandros, University of Gotheborg, Sweden) and ϕ_f = 0.28 in ethanol at 77 K (Prof. K. Schaffner, Max-Planck-Institute, Mülheim, FRG).

[11] (a) Kirby, E. P.; Steiner, R. F. *J. Phys. Chem.* **1970**, *74*, 4480. (b) Saltiel, J.; D'Augostino, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 6445. (c) Mirbach, M. F.; Mirbach, M. J.; Liu, K. L.; Turro, N. J. *J. Photochem.* **1978**, *8*, 299.

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Table IV. Singlet (ϕ^S) and Triplet (ϕ^T) Excitation Yields of Carbonyl Products Chemienergized in the Thermolysis of 1,2-Dioxetanes Determined by Means of Chemical Titration with 7,8-Benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene (BDT)

	singlet excitation yields ϕ^S, %			triplet excitation yields ϕ^T, %		
dioxetane	$\phi_{BTH}{}^{\infty}$,[a] %	obsd[b]	reported	$\phi_{BDTN}{}^{\infty}$,[c] %	obsd[d]	reported
1a	0.25 ± 0.02[e]	0.31 ± 0.04	0.25 ± 0.14 (ref 2)	10.0 ± 1.0[j]	15.6 ± 2.0	15–35 (ref 2, 22)
1b	0.12 ± 0.01[f]	0.14 ± 0.02	0.11 ± 0.03 (ref 17)	8.0 ± 1.0[k]	12.7 ± 2.0	15 ± 4 (ref 17)
1c	0.32 ± 0.02[g]	0.38 ± 0.04	0.019 (ref 18)	18 ± 10[l]	28 ± 15	22 ± 1 (ref 23)
1d	*h*		2 ± 1 (ref 19)	*m*		1.6 ± 0.1 (ref 23)
1e	0.27 ± 0.03[i]	0.30 ± 0.05	1.5 ± 0.2 (ref 2)	*m*		6.0 ± 0.5 (ref 2)

[a] BTH product quantitated by CGC with a 50-m OV101 column, operated at 130 °C oven temperature and a nitrogen gas flow of 1.1 mL/min; 2-methylnaphthalene as internal standard; extrapolated from a double reciprocal plot of ϕ_{BTH} vs. [BDT]. [b] Calculated by means of eq 17, using the temperature-dependent photochemical $\phi_r{}^S$ yields of Table I. [c] BDTN product (R_f = 245 s) quantitated by HPLC with a μ-Bondapak C_{18} reversed-phase column and 40:60 methanol/0.01 M aqueous phosphate buffer (pH 7.7) as eluant (flow rate 1.7 mL/min at 2500 psi); UV detection at 254 nm; *p*-aminoacetophenone as internal standard (R_f = 125 s); extrapolated from a double reciprocal plot of ϕ_{BDTN} vs. [BDT]. [d] Calculated by means of eq 18, using the photochemical yield $\phi_r{}^T$ = 65% of Table II. [e] [1a] = 0.110 M in benzene, thermolyzed at 80 °C for 1.5 h; [BDT] ranging between 0.1 and 0.005 M. [f] [1b] = 0.155 M in benzene, thermolyzed at 80 °C for 1.5 h; [BDT] ranging between 0.02 and 0.007 M. [g] [1c] = 0.116 M in benzene, thermolyzed at 80 °C for 1.5 h; [BDT] ranging between 0.04 and 0.007 M. [h] [1d] = 0.05 M in benzene, thermolyzed at 145 °C for 24 h and [BDT] = 0.05–0.005 M; no BTH product could be detected even under optimized CGC conditions. [i] [1e] = 0.03 M in benzene, thermolyzed at 120 °C for 2 h; [BDT] ranging between 0.03 and 0.008 M. [j] [1a] = 0.089 M in benzene, thermolyzed at 80 °C for 1.5 h; [BDT] ranging between 0.04 and 0.008 M. At these conditions BDTN decomposes (about 5% in 3 h). [k] [1b] = 0.047 M in benzene, thermolyzed at 80 °C for 1.5 h; [BDT] ranging between 0.04 and 0.008 M; saturated in dimedon. [l] [1c] = 0.147 M in benzene, thermolyzed at 80 °C for 1.5 h; [BDT] ranging between 0.02 and 0.006 M. [m] Not measured because BDTN is unstable at the high temperature (ca. 145 °C) required for the decomposition of dioxetane 1d and 1e.

plot (eq 21) is the product of the singlet–singlet energy transfer

$$\text{intercept/slope} = k_{et}{}^{SS}\tau_S \qquad (21)$$

constant ($k_{et}{}^{SS}$) and the lifetime of singlet excited acetone (τ_S). Taking $\tau_S \cong 2$ ns for singlet excited acetone[14] and knowing that this value is temperature independent,[15] we calculate that $k_{et}{}^{SS}$ is ca. $(3 \pm 1) \times 10^{10}$ s^{-1} since the intercept and the slope of Figure 1 are, respectively, 452 and 7.9. The diffusion rate constant in benzene at 80 °C is[16] 2.2×10^{10} s^{-1} so that singlet–singlet energy transfer for the process in eq 7 is diffusion controlled, a quite reasonable situation.

The singlet excitation parameters ϕ^S of the remaining dioxetanes **1b–f** were determined quite analogously from such double reciprocal plots of ϕ_{BTH} vs. [BDT]. The results are summarized in Table IV, together with the literature data. Some major discrepancies are clearly evident for the dioxetanes **1c–f**. Thus, while the reported value[18] for dioxetane **1c** from 9,10-diphenylanthracene energy transfer chemiluminescence[20] is ϕ^S = 0.019%, our value from chemical titration with BDT is ca. 20-fold higher, i.e., ϕ^S = 0.38 ± 0.04%. Since the dioxetane **1c** is one of the most susceptible toward catalytic dark decomposition, e.g., glass surfaces are very effective, it is possible that such nonluminescent decomposition of **1c** might be responsible for the lack of agreement between the two methods.

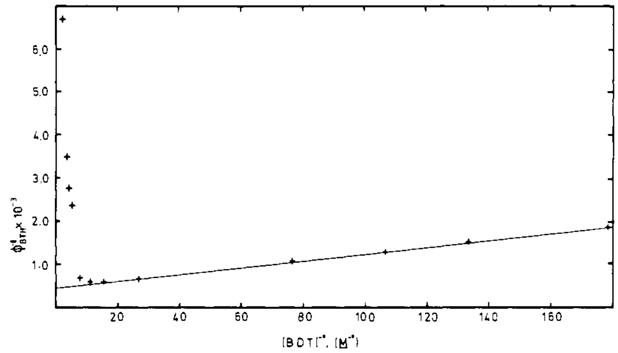

Figure 1. Chemical titration of excited singlet-state acetone with 7,8-benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene (BDT) in the thermolysis of tetramethyl-1,2-dioxetane (TMD).

Surprising at first was the lack of benzotricycloheptene (BTH) formation in the attempted BDT chemical titration of singlet excited adamantanone derived from the thermolysis of dioxetane **1d**.[19] The considerably higher thermolysis temperature (ca. 145 °C) of dioxetane **1d** was hardly responsible for the lack of BTH formation because both the azoalkane **BDT** and its denitrogenation product BTH were stable at these thermolysis conditions. Furthermore, a control experiment at these conditions with TMD produced the expected BTH product. Determination of the singlet

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(13) As logical mechanistic alternatives responsible for the decreasing chemical yield of benzotricycloheptene (BTH) with increasing azoalkane (BDT) concentration in the high [BDT] range, we considered (a) self-quenching of excited BDT singlets, (b) quenching of excited BDT singlets by the triplet-state product (the aziridine BDTN), (c) sensitized dioxetane decomposition by azoalkane triplets, (d) dark catalytic decomposition of the dioxetane by the triplet state product BDTN, and (e) dark catalytic decomposition of the dioxetane by the azoalkane BDT. Control experiments revealed that the photochemical yield $\phi_r{}^S$ of the BDT → BTH reaction was independent of [BDT], thereby discounting the BDT self-quenching mechanism (alternative a). Since the BDT fluorescence yield was not affected in the presence of authentic triplet state product BDTN, such quenching mechanism (alternative b) is unlikely in this context. The fact that triplet quenchers such as 2,5-dimethyl-2,4-hexadiene did not alter the observed kinetics of the dioxetane consumption implies that induced decomposition (alternative c) by azoalkane triplets (^{T}BDT*) is not important. Similarly, dark catalytic decomposition by the triplet-state product BDTN (alternative d) can hardly be operative since under triplet quenching conditions insignificant amounts of the aziridine BDTN have been produced to perform such dark catalysis. Although in the presence of authentic BDTN the rate of dioxetane consumption is accelerated, e.g., a twofold rate enhancement was observed over a ca. tenfold change in [BDTN], under the conditions of the singlet titration this effect is negligible. These facts leave us with the dark catalysis by the azoalkane BDT (alternative d) as a plausible mechanism. Indeed, the azoalkane BDT enhances the rate of dioxetane decomposition. Furthermore, the anomalous behavior in the double reciprocal plot (Figure 1) depends on the type of dioxetane. For the more sensitive dioxetane **1c** it occurs already at [**1c**] ≥ 0.015 M vs. [**1a**] ≥ 0.05 M. Finally, the observed parallelism in the dependence of ϕ_{BTH} (singlet titration) and ϕ_{BDTN} (triplet titration) on [BDT] suggests that the dark catalysis involves directly dioxetane.

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excitation energy of adamantanone by measurement of its absorption and fluorescence spectrum[21] showed that E_S is ca. 78–79 kcal/mol. Since for the azoalkane BDT we determined that E_S is ca. 79 kcal/mol, singlet–singlet energy transfer between singlet excited adamantanone and azoalkane BDT is inefficient, and therefore, the chemical yield of denitrogenation product BTH is too low for CGC detection. Control experiments reveal that the lower limit of BTH that can be detected with our CGC apparatus is $[\mathrm{BTH}] \sim 2 \times 10^{-5}$ M, corresponding to a lower limit in the singlet excitation yield of $\phi^S \sim 0.05\%$ that can be determined for dioxetanes by the present BDT chemical titration technique. Clearly, to date this method is the most sensitive and effective that has been reported for the determination of singlet excitation yields.

The 5-fold discrepancy in the ϕ^S results of dioxetane **1e** (Table IV), i.e., 0.30 ± 0.05% from the BDT titration vs. 1.5 ± 0.2%[2] from 9,10-diphenylanthracene energy transfer chemiluminescence,[20] can be readily explained on the basis of the above results for the dioxetane **1d**. Since singlet excited adamantanone goes undetected in the BDT chemical titration, the observed singlet excitation yield ($\phi^S = 0.30\%$) of dioxetane **1f** must correspond to chemienergized singlet excited benzyl formate. Thus, in the previous 9,10-diphenylanthracene determination[2] the $\phi^S = 1.5\%$ value represents the total singlet yield of chemienergized adamantanone and benzyl formate. This fact would imply a 5-fold differentiation in the singlet-state chemiexcitation in favor of adamantanone vs. benzyl formate, a reasonable result in view of the lower E_S value of adamantanone.

In summary, we can make the following conclusions concerning the present azoalkane (BDT) chemical titration of chemienergized singlet excited carbonyl products in the thermolysis of 1,2-dioxetanes: (a) The method is general for ketones, aldehydes, and esters, provided the singlet excitation energies (E_S) are greater than 79 kcal/mol. (b) The method is sensitive, allowing by means of capillary gas chromatographic analysis determination of singlet excitation yields (ϕ^S) equal or greater than 0.05% within an error of ca. 15%. (c) The method is spin state specific since singlet excitation affords exclusively denitrogenated products, i.e., 99% benzotricycloheptane (BTH) and 1% benzonorbornadiene; the small yield of benzonorbornadiene product can be neglected in the quantitative work. (d) The method is convenient and reliable, since the azoalkane BDT is readily available through synthesis, and like its denitrogenated product, BTH is stable at elevated temperatures to permit quantitative analysis by means of gas chromatography. (e) The method can be employed only in the low [BDT] range in view of the peculiar behavior of the double reciprocal plot of ϕ_{BTH} vs. [BDT] in the high [BDT] range (Figure 1).[13]

Triplet Excitation Yields of 1,2-Dioxetanes. Considerable greater difficulty was encountered with the quantitative analysis of the aziridine product BDTN that is produced in the triplet state specific chemienergization of azoalkane BDT by 1,2-dioxetanes. The hope that the BDTN product could also be quantitated by CGC and thereby enable the determination of both excitation parameters ϕ^S and ϕ^T directly by one and the same analytical method was unfortunately negated by the fact that the aziridine is thermally labile at the required conditions (ca. 130 °C) of the CGC analysis. Thus, HPLC had to be employed to establish the chemical yield of the BDTN product. Even here numerous practical problems were encountered. For example, on a silica column BDTN decomposed, while on a ±-Bondapak C_{18} reversed-phase column the methanol/water eluant led to hydrolysis of BDTN. However, when using as eluant a 40:60 mixture of methanol and 0.01 M phosphate buffer (pH 7.7), satisfactory results for the quantitation of BDTN could be obtained. As internal standard the basic *p*-aminoacetophenone served well our purpose.

The results of the triplet titrations of the dioxetanes **1a–c** are summarized in Table IV. Dioxetanes **1d** and **1e** could not be titrated with the present method in view of the already mentioned thermal instability of the aziridine BDTN at the excessive temperatures required for the thermolysis of these dioxetanes. For example, control experiments revealed appreciable (ca. 5%) decomposition of BDTN on heating at 80 °C for 3 h.

A few comments are worth mentioning concerning the ϕ^T data in Table IV. For example, for TMD a double reciprocal plot of ϕ_{BDTN} vs. [BDT] afforded a value of $\phi_{\mathrm{BDTN}}{}^{\infty} = 10.0 \pm 1.0\%$ as the intercept. By means of eq 18 and the photochemical yield $\phi_r{}^T = 65\%$ (Table II), we calculate that $\phi^T = 15.6 \pm 2.0\%$ for TMD. Although the reported value of ϕ^T for TMD range between 15 and 75%, the majority cluster around 35 ± 5%. While our present value falls within the observed range, it appears on the low side. However, recent results[22] using the 9,10-dibromoanthracene energy transfer chemiluminescence and the benzonorbornadiene chemical titration[23] methods have given consistently values of ϕ^T ranging between 15 and 35%. While we have as yet no logical explanation for the large variation, this does imply that our present value of $\phi^T = 15.6 \pm 2\%$ from the BDT chemical titration agrees with previous determinations well.

For comparison the rate constant $k_{\mathrm{et}}{}^{\mathrm{TT}}$ for the energy transfer of triplet acetone derived from TMD to azoalkane BDT (eq 12) was evaluated from the triplet titration data, following the method used for determining $k_{\mathrm{et}}{}^{\mathrm{SS}}$ (eq 21). Assuming a lifetime of $\tau_T \cong 10$ ns for triplet acetone[16] and using the values for the intercept and slope of the ϕ_{BDTN} vs. [BDT] double reciprocal plot of TMD, respectively, 8.8 and 0.2, affords $k_{\mathrm{et}}{}^{\mathrm{TT}} \sim 5 \times 10^8\ \mathrm{s}^{-1}$. Therefore, as expected the triplet–triplet energy transfer is ca. 50-fold slower than $k_{\mathrm{et}}{}^{\mathrm{SS}}$.

Considerable analytical problems were encountered with dioxetane **1b** in the triplet titration with the azoalkane BDT. Apparently the acetaldehyde produced a reaction product in this mixture which coincided in HPLC retention time with the aziridine product, for which quantitation by HPLC was essential in order to determine ϕ_{BDTH}. However, when the BDT chemical titration was performed in the presence of dimedon to trap the acetaldehyde, a reasonable value of ϕ^T was obtained which was within experimental error the same as the reported one (Table IV).[17]

Finally, the value of $\phi^T = 28 \pm 15\%$ that was obtained in the BDT chemical titration of dioxetane **1c** checks well our reported value of $\phi^T = 22 \pm 1\%$ by means of the benzonorbornadiene titration,[23] although the present experimental error is quite large. The reason for this wide error margin is of course again a practical problem of the present analytical method. No doubt, this analytical method could be improved and the error limits optimized, but in view of the fact that the benzonorbornadiene chemical titration[23] is a considerably more convenient and reliable technique for the determination of triplet excitation yields (ϕ^T), no further efforts were expended in improving our present triplet titration method with the azoalkane BDT.

Despite these practical limitations, it must be stressed that the BDT chemical titration has potential for the determination of triplet excitation yields. However, unquestionably its real advantage lies in the determination of singlet yields, for which no convenient, sensitive, and reliable chemical titration method was available until now.

Experimental Section

Instrumentation. The routine ^{1}H-NMR spectra were taken on a Hitachi-Perkin-Elmer R-24B spectrometer. Absorption spectra were re-

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[21] E_S of adamantanone was taken as the half-distance between the absorption maximum ($\lambda_{\max} = 304$ nm) and fluorescence maximum ($\lambda_{\max} = 423$ nm) in cyclohexane; the absolute fluorescence quantum yield of adamantanone was determined to be $\phi_f = 8.0 \times 10^{-3}$ (error ±10%) in cyclohexane at 25 °C (Prof. K. Sandros, University of Gotheborg, Sweden). As suggested by a reviewer, inefficient energy transfer could be also caused by steric effects. Such effects have been documented: cf. ref 14 of this paper and Janda, K.; Wettack, F. S. *J. Am. Chem. Soc.* **1972**, *94*, 305.

[22] Baader, W.; Zahn, A.; Zinner, K., unpublished results. The Stern–Volmer double reciprocal plots of the emission intensity and [DBA] are appreciably curved, so that interpolation of the intercept to evaluate the triplet yield ϕ^T at infinite [DBA] depends on the [DBA] range used. We have found values ranging between 10 and 50% for ϕ^T of TMD.

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corded on a Cary 17 spectrophotometer and fluorescence spectra on a Perkin-Elmer MPF-44B spectrofluorimeter.

The photochemical quantum yields ($\phi_r{}^S$ and $\phi_r{}^T$) were determined by means of an optical bench, equipped with a Hanovia 1000-W xenon–mercury high-pressure lamp, a Schöffler-Kratos monochromator, and a 1-cm UV sample cell. The photon flux was calibrated by means of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH)[9] and ferrioxalate as actinometers.[8]

The chemical yield of benzotricycloheptene (BTH) was measured on a Carlo Erba Fractovap 2900, employing a 50-m capillary column packed with OV-101 and operated at a split ratio of 1:50, injector, column, and detector temperatures of 175, 130, and 200 °C, respectively, and a nitrogen carrier gas flow of 1.1 mL/min. 2-Methylnaphthalene was used as internal standard.

The chemical yield of the aziridine BDTN was determined by HPLC on a Waters liquid chromatograph equipped with a model 6000-A pump and a 440 detector, employing a Waters μ-Bondapak C_{18} column, operated at an eluant flow rate of 1.7 mL/min and a pressure of 2500 psi. As eluant 40:60 methanol/0.01 M phosphate buffer (pH 7.7) was used with UV detection at 254 nm. *p*-Aminoacetophenone served as internal standard.

The dioxetane kinetics were carried out on a Mitchell-Hastings photometer,[24] equipped with a RCA PF1006 photomultiplier and a Lauda Thermostat NB-D8/17 for temperature control of the cell compartment. The Hastings-Weber scintillation cocktail[25] served as calibration standard of the light flux. Packard scintillation vials were used as reaction vessel. A Servogor 210 recorder registered the output signal of the kinetic run. The data were processed on a Tektronix 4051 desk computer.

The results and experimental conditions are collected in Tables I–IV.

Chemicals. All solvents were purified according to standard literature methods to reproduce the reported physical constants.

The 1,2-dioxetanes **1a–e** were prepared and purified according to the published procedures.[2] In all cases materials of better than 95% purity were used for the quantitative studies.

7,8-Benzo-2,3-diazatricyclo[4.3.0.$0^{4,9}$]nona-2,7-diene, the azoalkane BDT, mp 74–75 °C from petroleum ether (lit.[7] mp 74–75 °C), was prepared via cycloaddition of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and benzonorbornadiene and subsequent hydrolysis of the resulting urazole. The material is sensitive even to diffused daylight resulting in denitrogenation, so that all purifications and handling were performed in the dark. Purity checks by CGC and HPLC confirmed the absence of benzotricycloheptene (BTH) and aziridine (BDTN), respectively.

Authentic 2,3-benzotricyclo[3.2.0.$0^{4,6}$]hept-2-ene (BTH) was prepared from the azoalkane BDT via photodenitrogenation[7] and purified by GC collection on a Varian 920 instrument. BTH is stable at elevated temperatures up to 160 °C.

Authentic 7,8-benzo-2,3-diazatricyclo[4.3.0.$0^{2,9}$]nona-3,7-diene (BDTN) was prepared from azoalkane BDT via benzophenone-sensitized photorearrangement.[7] Repeated recrystallizations from 1:1 acetone/pentane afforded HPLC pure product, mp 143 °C dec (lit.[7] mp 140 °C dec). Control experiments confirmed that aziridine BDTN is easily hydrolyzed and decomposes readily above 80 °C.

General Procedure for the Chemical Titrations. Separate stock solutions of ca. 0.3 M dioxetane and of ca. 0.06 M BDT in benzene were prepared. By means of a calibrated microsyringe, 50-μL aliquots of the dioxetane and 10–100-μL aliquots of the BDT stock solution were transferred into a set of eight constricted test tubes and diluted with benzene to a total volume of 150 μL. After sealing, the ampules were heated in an oil bath, which was kept within 1 °C of the desired temperature, until complete consumption of the dioxetane. Details of the specific conditions for the individual dioxetanes are given in Table IV.

For the chemical titrations, 50-μL aliquots of the decomposed dioxetane solutions were taken, combined with 20 μL of internal standard solution in benzene (2-methylnaphthalene for the capillary GC analysis in the singlet titration and *p*-aminoacetophenone for the HPLC analysis in the triplet titration), and submitted to quantitative analysis. The conditions and results are summarized in Table IV.

Acknowledgment. We are grateful for the generous financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Professor K. Sandros (University of Gotheborg, Sweden) and Professor K. Schaffner (Max-Planck-Institute Mülheim, FRG) for measuring the fluorescence quantum yields.

Registry No. 1a, 35856-82-7; **1b**, 22668-10-6; **1c**, 84065-56-5; **1d**, 35544-39-9; **1e**, 82817-35-4; BDT, 70332-88-6; BTH, 7213-64-1; BDTN, 73834-11-4; nitrogen, 7727-37-9.

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Theoretical ab Initio Study of 1,3-Dipolar Cycloaddition of Fulminic Acid to Acetylene. Support for Firestone's Mechanism

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Received April 7, 1982

Abstract: A two-step pathway passing through a highly unsymmetrical transition state and an extended diradical intermediate has been investigated by ab initio computations with the 4-31G basis set and including various levels of electron correlation. Unrestricted Hartree–Fock and restricted Hartree–Fock plus 3 × 3 configuration interaction calculations are inadequate for the description of the energy surface around the diradical transition structure and for comparison of the concerted and diradical paths. A minimum of 4a′ and 3a″ occupied orbitals must be included in the CI treatment. With a multireference iterative perturbation technique using 17 reference determinants and ca. 2.4 million configurations, the extended diradical transition state was found to be 3.6 kcal mol^{-1} below the concerted, synchronous structure. While this energy difference is too small to favor one route unambiguously, the present calculations indicate that Firestone's diradical mechanism merits serious consideration, at least for the fulminic acid cycloaddition to acetylene and probably for other propargyl–allenyl type 1,3 dipoles.

The cycloadditions of 1,3 dipoles to olefins have been the object of a long controversy between Huisgen[2,3] and Firestone,[4–6] and among theoreticians. Huisgen classified the 1,3-dipoles into two catagories: the allyl type and the proparagyl–allenyl type, the latter having an additional π bond in the plane perpendicular to the allylic π system. In what follows we will refer to these as type I and type II, respectively.

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