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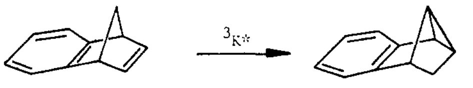
Chemical Titration of Thermally Generated Triplets[1]

Sir:

A unique feature of 1,2-dioxetanes is their selective production of triplet excited states on thermal decomposition.[2] The difficulty, however, has been the accurate and reliable quantitation of these chemienergized triplets. The very first attempts at chemically titrating triplets used cis,trans isomerization of stilbene or the dimerization of acenaphthene,[3] but unfortunately these titrimetric methods are not sufficiently spin specific and thus total excited-stated yields, i.e., singlets and triplets, are determined. In a now classical experiment, it was shown[4] that triplet acetone, chemienergized from tetramethyl-1,2-dioxetane (**1a**), selectively isomerizes fumaronitrile into maleonitrile. The drawbacks are that maleonitrile easily isomerizes thermally back to fumaronitrile during GLC analysis, resulting in large errors.[4,5]



(1)

2a **2b**

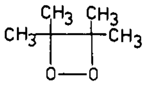
It is, therefore, not surprising that luminescence techniques, such as triplet–singlet energy transfer to 9,10-dibromoanthracene (DBA),[6] have been preferred over chemical titration methods for the quantitative determination of thermally generated triplets. Unfortunately, for low triplet excitation yields and for CIEEL-active substrates,[7] the DBA method can be unreliable.[8] Furthermore, a great deal of uncertainty still persists concerning the crucial triplet–singlet energy transfer efficiency, i.e., reported values range between 0.2 to 0.4,[9] leading to large errors in the DBA-measured triplet yields.

Clearly a convenient, reliable, and general chemical titrant is required for the quantitative determination of chemienergized triplet states. Ideally, the chemical titrant should (a) be spin specific, (b) have a high quantum efficiency of conversion to permit detection of low triplet yields, (c) form the photoproduct irreversibly so that photostationary corrections are unnecessary, (d) afford a volatile and thermally stable product to utilize GLC quantitation, and (e) be readily available. Fortunately, the triplet ketone-sensitized ($^3K^*$) di-π-methane rearrangement of benzonorbornadiene (**2a**) into the tricyclic product **2b** optimally[10] satisfies the above requisites (eq 1).

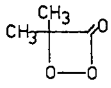
Table I. Thermally Derived Triplet Yields by Chemical Titration[a] with Benzonorbornadiene

dioxetane	[1], M	solvent	temp, °C	time, h	triplet yield, %[b]
1a	0.067	benzene	80	1	31 ± 1
1b	0.040	toluene	80[c,d]	1	1.1 ± 0.1
1c	0.10	benzene	145[e]	24	1.6 ± 0.1
1d	0.10	benzene	80	3	22 ± 1

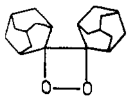
[a] For GLC conditions consult note 14. [b] Total triplet yields including direct and intersystem-crossing derived triplets. [c] Determined relative to dioxetane **1a** by duplicating exactly conditions of temperature, concentrations, time, etc., for **1b** that were used for **1a**; however, in view of the low thermal stability of **1b** vs. **1a**, clearly most of **1b** had already decomposed prior to reaching 80 °C. A control experiment for **1b** at 30 °C and 3 h gave the same results within experimental error as at 80 °C and 1 h. [d] Neither benzonorbornadiene (**2a**) nor its tricyclic isomer **2b** catalyze the decomposition of the α-peroxylactone **1b**, the most susceptible[15,16] member of the dioxetanes studied here. [e] Control experiments reveal that the photoisomerization quantum yield is independent of temperature, i.e., ~50%[10] over the temperature range employed in this work.



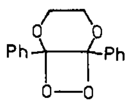
1a



1b



1c



1d

Presently, we demonstrate the general applicability and limitations of **2a** as chemical titrant of thermally generated triplet states derived from the 1,2-dioxetanes **1a–d.** With the help of tetramethyl-1,2-dioxetane (**1a**), which is more and more being used as relative standard for triplet yields,[11] we determine that the triplet acetone yield is 31 ± 1%, thus confirming that the DBA-determinated value of 30%[11] is reasonable. For the dimethyl α-peroxylactone (**1b**) we obtain a triplet acetone yield of 1.1 ± 0.1%, which establishes the lower limit of quantitative detectability of triplet excited states by this method.[12] The thermally quite stable diadamantylidene-1,2-dioxetane (**1c**) affords 1.6 ± 0.1% triplet adamantanone,[5] illustrating that the method can be used at temperatures up to ~150 °C. Finally, the dioxene-1,2-dioxetane **1d** gives 22 ± 1% triplet diester,[13] showing that this method is applicable to a variety of carbonyl triplet excited states. These results are detailed below.

Benzene solutions 0.067 M in dioxetane **1a** and variable molarity (0.285 to 0.713 M) in benzonorbornadiene (**2a**) were heated in a sealed tube at 80 °C until complete decomposition of **1a** (~60 min) and the ratio of **2b** to **2a** was determined by GLC[14] as a function of [**2a**]. A double inverse plot of the chemical yield of **2b** vs. [**2a**] afforded an intercept value of 6.5 ± 0.2 on triplicate analysis of three independent runs. Using the literature value of 0.50 for the photoisomerization yield of **2a** to **2b**, the triplet acetone yield from **1a** was found to be 31 ± 1% (Table I). This checks well with the 30% value determined by DBA fluorescence measurements[11] and matches the lower limit determined by fumaronitrile isomerization.[4] More significantly, our results suggest that a value of 0.20 for the triplet–singlet energy transfer efficiency for DBA[9] and the Hastings' calibration standard provide reliable triplet yield data, since these were used in the DBA fluorescence determinations.[11]

These encouraging results motivated us to determine the triplet acetone yield from α-peroxylactone **1b** because, at the time of commencing this study, no reliable values were known for α-peroxylactones.[12] Since **1b** can become involved in

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electron-exchange luminescence,[15,16] it was especially important to determine its triplet acetone yield by a chemical titration technique. Even if this complication were not applicable, the observed low triplet yield[8] would require correction for triplet states derived via intersystem crossing from singlet excited acetone.

With the benzonorbornadiene (**2a**) titrant, it was not possible via a double reciprocal plot to determine the triplet acetone yield from **1a.** The scatter of data points was too great to afford reliable intercepts. Consequently, at the highest, feasible [**1b**] of 0.04 M in toluene and [**2a**] of 0.04 M, the [**2b**]/[**2a**] ratio was determined relative to **1a** under identical conditions. Using a triplet acetone yield of 31% determined for **1a**, ten independent triplicate determinations gave a value of 1.1 ± 0.1% (Table I) of triplet acetone from **1b.** Our results check well with the recent determination via direct acetone phosphorence emission.[12] Furthermore, they establish the lower quantitative detection limit of triplet excitation by means of **2a** since the tricyclic photoisomer **2b** was just barely visible in the VPC trace.

The dioxetane **1c** was utilized to establish the upper temperature limit for our chemical titration method, since **1c** is to date still the most stable dioxetane.[5] Heating of benzene solutions 0.1 M in **1c** and variable concentrations (0.209 to 0.523 M) in **2a** in sealed tubes at 145 °C for 24 h secured complete decomposition. Determination of the [**2b**]/[**2a**] ratios by GLC as described for **1a**[14] and construction of a double reciprocal plot of the chemical yield of **2b** vs. **2a** gave intercept values of 125 ± 7. From this data and an isomerization efficiency of 50% for **2a** to **2b**,[10] we calculate a triplet adamantanone value of 1.6 ± 0.1% (Table I). Control experiments confirm that, under the thermolysis and GLC conditions, **2b** decomposes to the extent of only 3%, but it does not revert to **2a**, while **2a** is stable under these conditions. Furthermore, control experiments showed that the photoisomerization quantum yield is independent of temperature. Thus, the diadamantylidene-1,2-dioxetane **1c** represents the upper temperature limit for chemical titration of thermally generated triplets with benzonorbornadiene.

The determination of the triplet ester yield from the dioxenedioxetane **1d** was undertaken to illustrate the diversity of the method. Originally the di-π-methane rearrangement of **2a** into **2b** was shown[10] to be effective for ketones with triplet energies higher than 68 kcal/mol. Since the triplet energy of the diester derived from **1d** is expected to be ~79 kcal/mol,[17] **2a** should be applicable for the titration of the triplet ester derived from **1d.** Decomposition of benzene solutions 0.1 M in **1d** and at variable concentrations (0.209 to 0.523 M) in **2a** in sealed tube at 80 °C for 3 h gave an intercept value of 9.0 ± 0.2 from the double reciprocal plot of the chemical yield of **2b** vs. [**2a**]. This afforded a triplet diester yield of 22 ± 1% (Table I). Thus, this chemical titration method is not restricted to ketone triplet states. More importantly, dioxenedioxetanes are CIEEL active,[13] and the present chemical titration technique might be the only reliable method for the quantitation of such triplets.

In summary, the di-π-methane isomerization of **2a** to **2b** constitutes a convenient, reliable, and general method for the chemical titration of thermally generated triplet states. The method is sensitive, detecting triplet yields as low as 1%, can be used at elevated temperature up to 145 °C, and applies to a variety of carbonyl triplets such as ketones and esters as long as the triplet energies are 68 kcal/mol or greater.

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[18] (a) NIH Career Awardee, 1975–1980. (b) On study leave from the Suzuka College of Technology, Japan. (c) On study leave from the University of São Paulo, Brazil.

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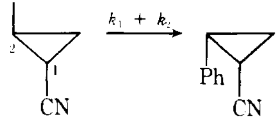
Secondary Deuterium Kinetic Isotope Effects in the Thermal Stereomutations of 1-Cyano-2-phenylcyclopropanes

Sir:

A recent kinetic study demonstrated that interconversion of *cis*- and *trans*-1-cyano-2-phenylcyclopropane occurs through one-center epimerizations at C(1) and C(2); no two-center processes contribute to the cis–trans isomerization, so that the experimentally observable rate constant for the reaction *dl*-**1a** → *dl*-**2a**, $k(\mathrm{t} \rightarrow \mathrm{c})$, is equal to the sum of two mechanistic rate constants ($k_1 + k_2$).[1,2]



1a **2a**

In conjunction with this study[1] we had an opportunity to measure two distinct secondary deuterium isotope effects[3] on the one-center epimerizations, starting with compounds **1b–d** or the corresponding cis isomers **2b–d**.

The deuterated systems **1b–d** and **2b–d** were available from or were synthesized by methods analogous to those employed in our earlier work.[1] The thermal equilibrations starting with