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LETTERS

Bond-Coupled Electron Transfer Reactions: Photoisomerization of Norbornadiene to Quadricyclane

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In this paper, we report on the bond coupled electron transfer (BCET) isomerization reaction of norbornadiene (NB) to quadricyclane (Q). We have used several triplet sensitizers to examine electron and energy quenching by NB. In the case of acetophenone, energy transfer generates the detectable ^{3}NB, which rearranges to give ^{3}Q which relaxes to Q. Using chloranil, benzoquinone, and 2,5-dichlorobenzoquinone as triplet sensitizers, the triplet ion pairs are generated, but cannot access either ^{3}NB or ^{3}Q, and so the ion pair undergoes return electron transfer to the ground state. However, with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride as the triplet sensitizer, the triplet ion pair is generated, but can undergo BCET to ^{3}Q efficiently, which then relaxes to Q. To our knowledge, this is the first example of an efficient electron-transfer mechanism to photoisomerize NB to Q without the intermediacy of ^{3}NB. Consequently, in the valence isomerization of NB to Q, it is possible to directly access the NB-Q triplet surface by controlling the energy of the triplet ion pair photogenerated, and in effect, the quantum yield can be modulated.

Introduction

Return electron transfer (RET) processes in photoinduced electron transfer reactions are typically viewed as undesirable energy-wasting steps. Indeed, a considerable amount of work has been directed toward strategies to increase the efficiencies of photoinduced electron transfers by decreasing the rate of RET, or increasing the rates of useful competing processes such as ion pair separation or follow-up ion radical reactions.[1] Instead of RET competing with the useful processes, however, an alternative approach would be to have RET itself do useful work. We recently reported on such a process with 1,2-diphenylcyclopropane in which bond-coupled electron transfer (BCET) resulted in cis−trans isomerization via initial cleavage of the ring to form a 1,3-biradical.[2] In fact, BCET can be significantly faster than RET and result in high quantum efficiencies for isomerization. In this paper, we now report on the bond coupled electron-transfer isomerization reaction of norbornadiene (NB) to quadricyclane (Q).

The mechanism of valence isomerization of norbornadiene to quadricyclane has been extensively studied.[3] Triplet sensitization of norbornadiene generates its triplet state, ^{3}NB, which undergoes adiabatic isomerization to the triplet state of quadricyclane, ^{3}Q, which very rapidly decays to its ground state, Scheme 1.[4]

On the basis of our previous work, we postulated that valence isomerization may also be possible from the triplet ion pair state, $^3(A^{\bullet-}/NB^{\bullet+})$, directly to ^{3}Q via BCET in competition with RET. Herein, we detail our mechanistic investigation of BCET isomerization of NB using a variety of triplet sensitizers.

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SCHEME 1

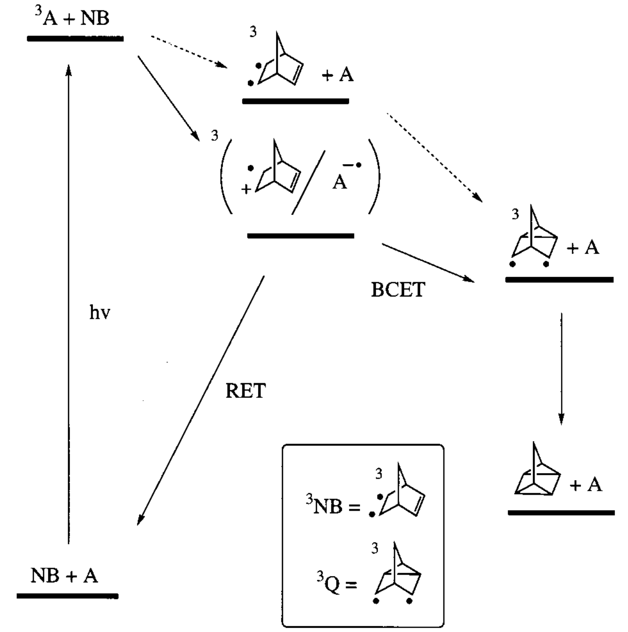


TABLE 1

sensitizer	Φ	E_{red}[a]	E_T[b]	E_{irp}[c]	ΔG_{et}(³sens)[d]
acetophenone	>0.9	−1.85	73.6	82.8	+9.2
BTDA	>0.9	−0.81	65.9	58.8	−7.1
TCB	0.34	−0.65	64.8	55.1	−9.7
BQ	0.0	−0.51	53	51.9	−1.1
DCBQ	0.0	−0.18	50	44.3	−5.7
CHL	0.0	+0.02	50	39.7	−10.3

[a] in V (vs SCE), see ref 16. [b] kcal/mol, see ref 17. [c] kcal/mol, see text. [d] kcal/mol, $\Delta G_{et} = E_{irp} - E_T$.

Results

Photoacoustic Calorimetry. Triplet sensitization of NB (0.5M) using acetophenone in CH_2Cl_2 results in two heat depositions. The first deposition yields a transient with energy of 61 kcal/mol relative to NB and ground-state acetophenone, and a lifetime of 7.2 ns. The overall energy retained in the photoacoustic experiment is 23.3 kcal/mol.[5] These results are in excellent agreement with those previously obtained by Caldwell[6] and suggest the transient is ^{3}NB, which decays to Q with quantum efficiency >0.9. The ^{3}Q was not detected, presumably because of its short lifetime, <1 ns.

Triplet sensitization of NB with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), results in only one heat deposition, with an overall energy storage of 22.5 kcal/mol. This requires that ^{3}NB is not formed but Q is produced rapidly, < 1 ns, and efficiently. Triplet sensitization of NB using 1,4 benzoquinone (BQ), 2,5-dichloro-1,4-benzoquinone (DCBQ), and chloranil (CHL) also result in only one heat deposition but no energy is stored which implies that neither ^{3}NB nor Q are formed using these sensitizers. In addition, both NB and these sensitizers are regenerated which indicates no chemical reaction occurs.

Quantum Yields Measurements. Quantum yields for isomerization of NB to Q were determined using several triplet sensitizers and are given in Table 1. For acetophenone and BTDA, the quantum yields for isomerization are quite high >0.9. In contrast, BQ, DCBQ, and CHL do not effect isomerization. A quantum yield of 0.34 was obtained using the triplet state of 1,2,4,5-tetracyanobenzene, TCB. The triplet energies of the sensitizers and the ion pair energies are given in Table 1. The ion radical pair energies are calculated according to $\Delta G = E_{ox}(NB/NB^+) - E_{red}(A^-/A) - e^2/\epsilon r$ using the oxidation potential of NB, 1.54 V vs SCE,[7] the reduction potentials of A,[16] and the Coulomb term, ~ 0.2 V in $CDCl_3$.[8]

Laser Flash Photolysis. The rate of quenching of the triplet state of the sensitizers was measured by nanosecond absorption spectroscopy. Using the absorption of the triplet state of the sensitizers, the rate of decay was measured as a function of NB concentration. The triplet states of all the triplet sensitizers were quenched by NB at approximately diffusion controlled rates, $\sim 5 \times 10^9$ M^{-1} s^{-1}. Quenching of the triplet states of acetophenone and BTDA with NB in $CDCl_3$ yielded no observable transient on either the nanosecond or picosecond time scale. However, quenching of the CHL triplet ($\lambda_{max} = 510$ nm) produced a transient ($\lambda_{max} = 450$ nm) with a lifetime < 5 ns. We assign this transient to be $CHL^{-\bullet}$ on the basis of its known spectrum, and is formed by electron transfer from NB to ^{3}CHL.[9]

Discussion

The rate of reaction of NB with triplet acetophenone occurs at diffusion control and generates ^{3}NB as demonstrated by PAC. The reaction presumably occurs via energy transfer and not by sequential electron transfers as the initial transfer to form the ion pair is endothermic by ~10 kcal/mol, Table 1. ^{3}NB has a lifetime of ~7 ns and an energy of 61 kcal/mol and decays to Q with high efficiency presumably via ^{3}Q which is not observed. These results are in good agreement with those of Caldwell.[6]

In contrast, the reactions of NB with ^{3}BQ, ^{3}DCBQ and ^{3}CHL, which occur at diffusion control, do not yield ^{3}NB as no transient is observed by PAC. In addition, quantum yield measurements and PAC show that no photoisomerization of NB to Q occurs. Quenching of ^{3}CHL by NB does produce $CHL^{-\bullet}$, which implies initial electron transfer to give the triplet ion pair, $CHL^{-\bullet}/NB^+$. Decay of this ion pair occurs rapidly, <5ns, via return electron transfer to regenerate NB.

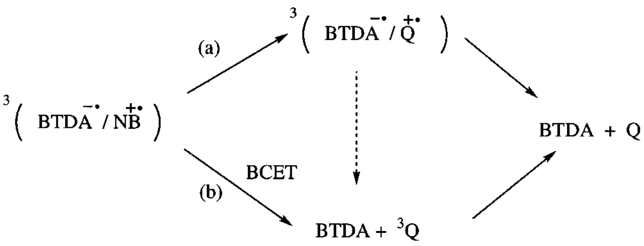
The reaction of NB with ^{3}BTDA is significantly more interesting than with the other sensitizers. Whereas quenching occurs at diffusion control and yields Q efficiently, it does not generate ^{3}NB. So although both triplet energy transfer and electron transfer are energetically favorable (see Table 1), triplet energy transfer apparently does not occur. In fact, other sensitizers with similar triplet energies to BTDA but which cannot react with NB by electron transfer do not efficiently isomerize NB.[10] We postulate that electron transfer occurs instead to initially form the triplet $BTDA^{-\bullet}/NB^+$ ion pair. Unfortunately, picosecond absorption spectroscopy experiments showed the quenching of ^{3}BTDA (<100 ps, 1M NB), but no evidence for the formation of the ion pair. However, this can be explained if the lifetime of the ion pair is short, <100ps. If the ion pair is indeed formed, its decay must yield Q efficiently, but how does this occur?[12]

Assuming initial formation of the triplet ion pair, two reasonable pathways could explain the formation of Q, Scheme 2.[13]

Pathway (a) involves initial isomerization of $NB^{+\bullet}$ to $Q^{+\bullet}$ followed by return electron transfer to yield either ^{3}Q or Q directly. Pathway (b) involves concerted isomerization and return electron transfer to generate ^{3}Q, which then decays to Q via intersystem crossing.

Pathway (a) requires that the unimolecular rearrangement of $NB^{+\bullet}$ to $Q^{+\bullet}$ must be extremely rapid as given by the lifetime of the triplet $BTDA^{-\bullet}/NB^+$ ion pair, <100 ps. However, this rearrangement is reported to occur on the microsecond time

SCHEME 2



scale,[11] effectively ruling out this pathway. Moreover, the rearrangement rate should not be dependent on sensitizer. Using CHL as a triplet sensitizer, in which the ion pair is observed, no rearrangement occurs. This observation cannot be explained by pathway (a).

The bond coupled electron transfer pathway (b) can reasonably explain all the experimental observations. The triplet state of Q has not been directly observed and its energy has not been determined. However, ab initio calculations have predicted its triplet energy to be 57.5 kcal/mol above NB and 23.6 kcal/mol above Q,[14] and it is also known that ^{3}Q efficiently yields Q.[15] Consequently, only triplet ion pairs with energies near or above 57.5 kcal/mol can access ^{3}Q. Of the triplet sensitizers employed, only BTDA yields a triplet ion pair with sufficient energy to efficiently produce ^{3}Q. Sensitizers BQ, DCBQ and CHL produce ion pairs whose energies are significantly below ^{3}Q and so they decay by RET with no net observable isomerization of NB. The TCB$^{-\bullet}$/ NB^{+} ion pair, 55.1 kcal/mol, apparently can access ^{3}Q in competition with RET. In addition, the short lifetime of the BTDA$^{-\bullet}$/NB$^{+\bullet}$ ion pair can be rationalized as occurring by a spin allowed, slightly exothermic bond coupled electron-transfer reaction.

Conclusions

In photoinduced electron transfer reactions, RET has always been viewed as a problem to overcome. However, RET can be rendered useful by coupling electron transfer to a chemically productive event involving bond-breaking or bond-making. In the valence isomerization of NB to Q, it is possible to directly access the NB-Q triplet surface by controlling the energy of the photogenerated triplet ion pair and, in effect, the quantum yield can be modulated.

We have used several triplet sensitizers to examine electron and energy quenching by NB. In the case of acetophenone, energy transfer generates the PAC detectable ^{3}NB, which rearranges to give ^{3}Q followed by relaxation to Q. Using CHL, BQ, and DCBQ as triplet sensitizers, the triplet ion pairs are generated, but cannot access either ^{3}NB or ^{3}Q and so undergo RET to the ground state. With BTDA as the triplet sensitizer, electron transfer also generates a triplet ion pair, but this ion pair can undergo efficient BCET to ^{3}Q, which then relaxes to Q. To our knowledge, this is the first example of an efficient electron-transfer mechanism to photoisomerize NB to Q without the intermediacy of ^{3}NB.

Experimental Section

Materials. Spectroscopic grade solvents were used as received. $CDCl_3$ was stored over poly(4-vinylpyridine). Ferrocene, 2-hydroxybenzophenone, 3,3′,4,4′-benzophenone-tetracarboxylic dianhydride (BTDA), benzophenone, and TCB were recrystallized several times from appropriate solvents. CHL, BQ, and DCBQ were recrystallized and/or sublimed prior to use. Norbornadiene, quadricyclane, and acetophenone were distilled prior to use.

Absorption Spectroscopy. Nanosecond laser plash photolysis experiments were carried out using an excimer (Lambda Physik Lextra 50, XeCL,308 nm) pumped dye laser(Lambda Physik LPD 3002, 7ns pulse width) as the excitation source. Tuning of the excitation wavelength was possible through a dye laser chamber (Lambda Physik). Transient absorptions were monitored at right angles to excitation with a conventional xenon lamp, monochromator, photomultiplier tube arrangement. The signal from the multiplier tube was recorded and digitized with a Tektronix TDS 620 digitizing oscilloscope and then passed to a microcomputer for storage and analysis. The excitation beam energy was typically attenuated to less than 2−3 mJ per pulse, and appropriate long pass filters were placed on either side of the sample to prevent analyzing light photolysis.

Picosecond laser flash photolysis experiments were carried out using a Continuum model PY-61C-10 Nd:YAG laser, which operates at 10 Hz and uses active mode locking and cavity dumping. The laser produces ca. 60 mJ at 1064 nm, which can be converted into ca. 30 mJ at 532 nm after appropriate frequency conversion in KDP. The residual 1064 nm is separated from the harmonics using dichroic mirrors and is directed to an optical delay. The delay line consists of a solid BK-7 retroreflector mounted on a 4-foot long Velmex model MB4051K2J−S4 translation stage. The excitation and analyzing beams pass through Vincent Associates model 225L2A0Z5 shutters before hitting the sample. The two monochromatic beams that exit the monochromator corresponding to the sample and the reference signals are directed: (i) for spectra analysis, toward a CCD model which is connected to the computer for storage and analysis, (ii) for kinetic analysis, toward Hamamatsu model HC120−5 PMT. The outputs of the PMT are electronically filtered and digitized using a LeCroy model 9304 175 MHz oscilloscope, which is connected to the computer for storage and analysis.

Photoacoustic Measurements. PAC measurements were made using a front face irradiation cell with 347 nm excitation provided by a P. R. A. model LN1000 laser. Data were collected with a 10 MHz transducer (Panametrics A611S−SB) with a 25 μm shim. The optical density of the transducer wave was matched to that of the experimental wave. Each measurement consisted of 50 averaged shots. Ferrocene and 2-hydroxybenzophenone were used for the T-waves. CH_2Cl_2 was used as the solvent.

Quantum Yields Measurements. Quantum yields measurements were made using an optical bench consisting of an Oriel 66002 Universal Lamp housing equipped with an Oriel 6283 200W Hg lamp, connected to an Oriel 68805 power supply, and mounted on Oriel 11150 high stability optical bench. Attached in series to the lamp housing was an Oriel 71430 shutter, and an Oriel 6194 Liquid Filter filled with water, and Schott Glass Technologies UG 11 band-pass filter.

A quartz cuvette equipped with a Teflon stopcock and a Teflon coated stir bar was charged with 2.0 mL of a solution of the sensitizer (OD > 1.0), norbornadiene (0.01−0.1 M) and norbornane (0.1−1 mM) as the internal standard, in $CDCl_3$. The solution was purged with a stream of argon and photolyzed using an appropriate band-pass filter. The solution was then analyzed by GC using an Altech Econo-Cap SE-30 column. The quadricyclane was quantified using norbornane as an internal standard after appropriate response factor correction. For TCB experiments, 1.2 mM NB was used, and the quantum yield was corrected for interception of the TCB singlet by NB.[2]

Actinometry was performed using Aberchrome 540 (*J. Chem. Soc., Perkin Trans. II* **1981**, 341). A 2.0 mL solution of Aberchrome 540 (0.005 M) in toluene was irradiated and the moles of photoproduct were determined from the change in optical density at 494 nm and the extinction coefficient (8200 $M^{-1}cm^{-1}$). The known quantum yield of photoproduct (0.20) was used to calculate the photon flux.

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(12) Photoisomerization of NB to Q occurs using 9,10-anthraquinone, AQ, as the sensitizer. The quantum yield for isomerization is high, 0.9. Picosecond absorption experiments show ^{3}AQ is rapidly quenched by NB, but the ion pair if formed is not observed. PAC experiments indicate the formation of an intermediate with a lifetime of ~7 ns. This is consistent with the formation of ^{3}NB via electron transfer from the ion pair or energy transfer directly from ^{3}AQ. However, the partitioning of the heat depositions between the fast and slow components in the PAC experiments suggest that ^{3}NB is not formed with high efficiency (<0.9). The simplest explanation that fits the PAC data is that the ion pair formed via initial electron-transfer yields *both* ^{3}NB and ^{3}Q directly. This is consistent with the fact that the ion pair energy (~61 kcal/mol) is close to that of ^{3}NB and so, unlike BTDA, the $AQ^{-\bullet}/NB^{+\bullet}$ ion pair can form in competition with ^{3}Q. This does not occur with BTDA because the ion pair is slightly lower in energy than that with AQ.

(13) A third pathway is plausible which involves the concerted isomerization and return electron transfer directly to Q without the formation of ^{3}Q. Although we cannot exclude this pathway, it does requires rearrangement and spin forbidden return electron transfer to occur simultaneously.

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