was heated to reflux and 36 μL (432 mmol) of concentrated hydrochloric acid was added. After 15 min at reflux, the suspension was cooled to room temperature and filtered. The resulting white powder (7.7 mg, 24.1% yield) was identical by ^{1}H NMR, MS, and mixed melting point to the spiroepoxide prepared above.

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Registry No. 4, 91158-67-7; TX, 492-22-8; methyl methacrylate, 80-62-6; dimethylaniline, 121-69-7; triethylamine, 121-44-8; dibutylamine, 111-92-2; *tert*-butylamine, 75-64-9; tri-*n*-butylstannane, 688-73-3.

Olefin Oxidation Initiated by a Ground-State Electron Acceptor

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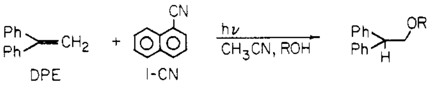
The reaction between 1,1-diphenylethylene (DPE) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF$_4$) in air-saturated acetic acid mimics the photochemical electron-transfer oxidation of this olefin. However, the mechanism of the photooxidation is apparently quite different from that observed for the TCNQF$_4$-mediated reaction. In the latter case a peroxide-initiated free-radical oxidation occurs.

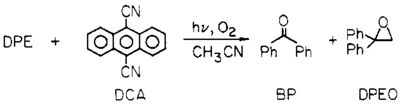
The reaction of olefins with powerful electronically excited electron acceptors frequently provides pathways for reactions which are not observed under other conditions. In this regard, Hixson[1] was the first to observe photochemical anti-Markovnikov addition of an alcohol initiated by excitation of a cyano-substituted aromatic chromophore. The potential of this process was developed more fully by Arnold and co-workers[2] who found, for example, that irradiation of an alcoholic solution of 1-cyanonaphthalene (1-CN) containing 1,1-diphenylethylene (DPE) gives good yields of ethers,[2b] eq 1.



(1)

The mechanism for this reaction is suggested to involve first the transfer of an electron from DPE to 1-CN*[1] giving DPE$^{+\cdot}$ and 1-CN$^{-\cdot}$. In subsequent steps the alcohol adds to DPE$^{+\cdot}$ to give the more stable benzylic radical, the radical is reduced by 1-CN$^{-\cdot}$ to give an anion, and, finally, the anion is protonated to give the observed ether. This general sequence has been invoked for other nucleophiles and other olefins as well.

When O$_2$ is present in solution DPE$^{+\cdot}$ can be diverted to other products. Oxidation of DPE by irradiation of its SbCl$_5$ complex in O$_2$-saturated CH$_2$Cl$_2$ gives a dimeric cyclic peroxide.[3] Foote[4] and later Schaap[5] have shown that electron-transfer photooxidation of DPE in acetonitrile solution gives benzophenone (BP) and diphenylethylene oxide (DPEO), eq 2. The mechanism for this reaction is thought to involve trapping of DPE$^{+\cdot}$ by O$_2^{-\cdot}$ generated from reduction of O$_2$ by DCA$^{-\cdot}$. Foote and Eriksen[4b] report that when this reaction is carried out in methanol there is a competition between addition and oxidation.



(2)

Similar mechanisms have been considered to explain the photooxidation of DPE initiated by irradiation of solid-state semiconductors.[6] In this case reduction of the semiconductor gives DPE$^{+\cdot}$ which may be bound to the surface while it reacts to become eventually BP and DPEO.

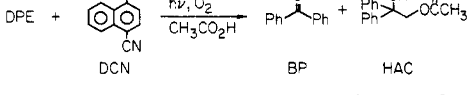
In the reactions described above it is reasonable that an exciplex, or an excited charge-transfer complex, is the precursor to the key radical ion intermediates. It is well-known that olefins such as DPE form ground-state "charge-transfer" complexes with suitable electron acceptors. We undertook this investigation to determine if these ground-state complexes can similarly serve to initiate reactions of olefin radical cations.

Results

Our investigation centers on the reactions of DPE in acetic acid. The electron-transfer photochemistry of DPE has not been reported previously in this solvent; we examined it briefly and compared it with the thermal reaction.

The fluorescence of 1,4-dicyanonaphthalene (DCN) in acetic acid is quenched by DPE. The Weller equation[7] predicts that electron transfer to form DCN$^{-\cdot}$ and DPE$^{+\cdot}$ during this process is favorable by ca. 10 kcal/mol.

Photolysis of an air-saturated solution of DCN and DPE at 350 nm gives benzophenone and the hydroxyacetate (HAC), in a ratio of ca. 3:1, eq 3. These are the expected



(3)

products based on analogy to the earlier work on related systems in methanol.[4b] In particular, we have shown that DPEO is converted rapidly to HAC in acetic acid.

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[1] (a) Hixson, S. S. *Tetrahedron Lett.* **1971**, 4211. (b) Hixson, S. S. *J. Am. Chem. Soc.* **1972**, *94*, 2505.

[2] (a) Neunteugel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. (b) Arnold, D. R.; Maroulis, A. J. *Ibid.* **1976**, *98*, 5931. (c) Shigemitsu, Y.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 407. (d) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535.

[3] Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. *Aust. J. Chem.* **1978**, *31*, 1737.

[4] (a) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391. (b) Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 6083.

[5] Schaap, A. P.; Zaklika, K. A.; Kaskar, B.; Fung, L. W.-M. *J. Am. Chem. Soc.* **1980**, *102*, 389.

[6] (a) Fox, M. A.; Chen, C.-C. *J. Am. Chem. Soc.* **1981**, *103*, 6757. (b) Fox, M. A.; Chen, C.-C. *Tetrahedron Lett.* **1983**, *24*, 547. (c) Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Ibid.* **1980**, *21*, 467.

[7] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

0022-3263/84/1949-3356$01.50/0

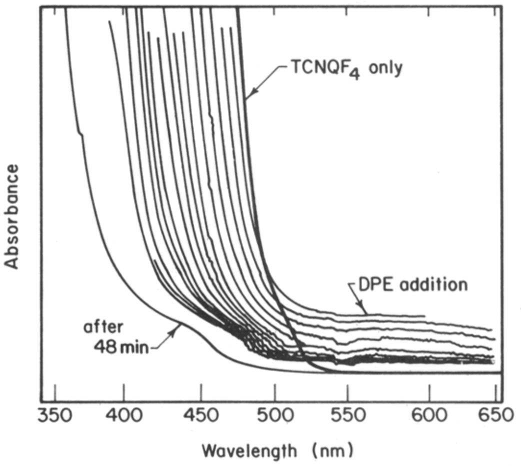
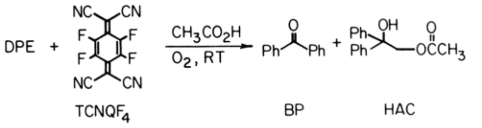


Figure 1. Absorption spectra recorded for an air-saturated solution of DPE and $TCNQF_4$ in acetic acid. The spectra were measured at ca. 1-min intervals.

Precisely the same products are formed from the ground-state reaction of DPE with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$) in air- or oxygen-saturated acetic acid, eq 4. The yields of HAC and



(4)

BP in this reaction depend on the DPE concentration. When the starting concentration of DPE is ca. 0.2 M, the yield of BP is ca. 300% and that of HAC is ca. 100% based on the amount of $TCNQF_4$ consumed. These findings seem to indicate that the thermal reaction does indeed mimic the photochemical process. However, a detailed investigation of the mechanism reveals that these reactions may be only superficially related.

A new, broad, structureless absorption band with a maximum at 575 nm is formed when DPE and $TCNQF_4$ are mixed in deoxygenated acetic acid, Figure 1. The species responsible for this absorption is not stable, but reacts under these conditions over several minutes. Similar results are obtained in air-saturated solutions.

The intensity of the absorption band at 575 nm and the lifetime of the complex are both directly proportional to the concentration of DPE. A Benesi–Hildebrand plot[8] of these data indicates that the species responsible for the absorption band is a 1:1 complex of $TCNQF_4$ and DPE with an apparent formation constant (K_c) of 0.36 M^{-1}.

The formation of BP and HAC does not coincide in time with the consumption of $TCNQF_4$. In a typical reaction the $TCNQF_4$ is completely consumed in ca. 15 min, but analysis by gas chromatography shows that only a small fraction of the DPE oxidation products has been formed at this time. The oxidation products, BP and HAC, grow into the reaction mixture with a half-life of about 10 h. This result indicates that these products are formed from a metastable intermediate that is generated by reaction of $TCNQF_4$ and DPE.

There are two general routes by which an intermediate may go on to form BP and HAC. In the first, the intermediate decomposes unimolecularly to form the products and already contains a protooxidized DPE, eq 5. In the second, the intermediate serves as an initiating agent that converts unconsumed DPE to oxidation products, eq 6.

$$TCNQF_4 + DPE + O_2 \longrightarrow [I] \longrightarrow BP + HAC \qquad (5)$$

$$TCNQF_4 + DPE + O_2 \longrightarrow [I] \xrightarrow[O_2]{DPE} BP + HAC \qquad (6)$$

These possibilities were tested with several experiments.

A deuterium tracer experiment was performed to determine if the HAC comes from DPE consumed in the initial reaction (eq 5) or in subsequent reaction of the intermediate I (eq 6). A solution of DPE and $TCNQF_4$ was prepared and allowed to react in the normal way for 15 min during which time the $TCNQF_4$ is completely consumed. Next, a quantity of DPE-d_{10} equivalent to the amount of DPE present initially was added to the reaction mixture. The HAC formed eventually by this reaction was analyzed by mass spectroscopy and shown to be a 60:40 mixture of HAC and HAC-d_{10}. This result is inconsistent with the reaction scheme shown in eq 5 and supports the sequence outlined in eq 6.

Similarly, we determined that O_2 is required by the intermediate to convert DPE to BP and HAC. When the O_2 is removed from the reaction solution by freeze–pump–thaw degassing 15 min after the reaction is initiated ($TCNQF_4$ consumed) the oxidation products are not formed in high yield. However, once O_2 is readmitted to the solution, even many hours after the reaction normally would have reached completion, the oxidation begins, and HAC and BP are formed. This result also supports the mechanism outlined in eq 6 and additionally indicates that O_2 "activates" the intermediate.

The results seem to support a free-radical oxidation of DPE that is somehow initiated by an intermediate formed from $TCNQF_4$. Indeed, DPE is converted to BP and HAC in acetic acid by conventional free-radical initiators such as 2,2-azobis(isobutyronitrile) (AIBN). To examine this further we studied the effect of 2,6-di-*tert*-butyl-*p*-cresol (BHT), a well-known free radical inhibitor, on the $TCNQF_4$-initiated oxidation of DPE.

Several solutions were prepared that contained DPE, $TCNQF_4$, and BHT (0–0.02 M). The BHT does not inhibit the initial reaction that consumes $TCNQF_4$. However, 0.02 M BHT reduces the ultimate yield of both BP and HAC by a factor of ca. 6. This finding strongly supports the free-radical nature of the oxidation and also indicates that this process does not involve a long radical kinetic chain.

Discussion

Our findings indicate that a complex is formed between DPE and $TCNQF_4$. A related complex has been reported for $TCNQF_4$ and styrene.[9] In this case the complex is stable at room temperature, but heating it initiates a copolymerization reaction. We suspect that a related sequence operates for DPE and $TCNQF_4$ in acetic acid. That is, the complex reacts with the acid to give a covalently bound intermediate (I). We can only speculate on the structure of this intermediate since we have not been able to completely characterize the $TCNQF_4$-containing product(s). However, analysis by mass spectroscopy shows that at least a portion of the $TCNQF_4$ has added DPE and acetic acid. On the basis of these observations we suggest that the first irreversible step in the reaction sequence is addition of acetic acid to the complex to form intermediate I (eq 7, Scheme I). The data indicate that this process is complete at room temperature in ca. 15 min.

The oxidation of DPE does not proceed in the presence of intermediate I when O_2 is removed from the solution. This suggests that a reaction between the intermediate and

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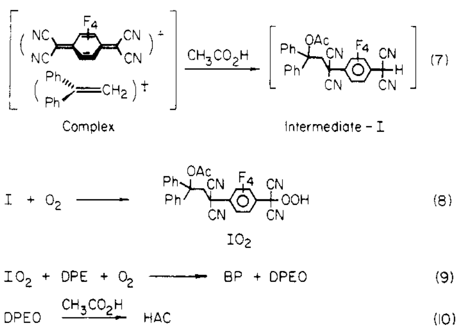
[8] Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

[9] Iwatsuki, S.; Itoh, T. *Macromolecules* **1982**, *15*, 347.

Scheme I



O_2 creates the ultimate oxidant. Just such a reaction has been observed between nitriles and O_2 to give α-hydroperoxy nitriles.[10] This transformation is shown in eq 8 on Scheme I and is likely to proceed first by reversible ionization of intermediate I.

The penultimate step in the proposed mechanism is the reaction of the oxidized intermediate IO_2 with DPE. This process also is well precedented. Rebek[11] has observed similar reactions of electron-poor hydroperoxides with a variety of olefins. In the present case, the conversion of DPE to BP and DPEO (ultimately to HAC) by IO_2 must occur at least in part by a free radical chain reaction since yields greater than 100% are obtained.

The findings described above make it quite clear that although the products are the same, the mechanism for oxidation of olefins by electronically excited electron acceptors may be quite different from that for ground-state acceptors. However, the mechanism of the photooxidation in many cases is not well defined, and care should be taken in the analysis of these transformations to consider processes related to those shown in Scheme I.

Experimental Section

General Methods. DPE (Aldrich) was distilled before use. DPE-d_{10} was prepared from bromobenzene-d_6 and ethyl acetate according to a procedure for DPE.[12] $TCNQF_4$ was prepared according to Wheland[13] and recrystallized from CH_2Cl_2; its purity was verified by elemental analysis. DCN was prepared as previously described.[14] HAC was prepared according to Mango and Bonner:[15] mp 91.5–92.0 °C (lit.[15] mp 93–93.5 °C); NMR (220 MHz, $CHCl_3$) δ 7.55–7.10 (m, 10), 4.67 (s, 2), ~3 (s, 1), 2.02 (s, 3); mass spectrum (70eV, electron impact), m/z (relative intensity) 256 (<1), 196 (2), 184 (19), 183 (100), 106 (10), 105 (100), 77 (66), 51 (13), 43 (36). 2,2-Diphenyloxirane (DPEO) was prepared by the procedure described by Eliel and Delmonte.[16]

Instrumentation. Gas chromatography was performed on a Varian 3700 instrument with a 6 ft × $^1/_8$ in. glass column packed with 5% SE-30 on Gas Chrom Q with tetradecane as internal standard. A Hewlett-Packard 3390 A Integrator was used to record and integrate the traces. Liquid chromatography was performed by using a Perkin-Elmer Series-2 Liquid Chromatograph equipped with an LC-75 Spectrophotometric Detector (variable wavelength). Analytical columns were either silica A (Perkin-Elmer) 0.26 × 25 cm, C-8/10 (Perkin-Elmer) 0.45 × 25 cm, or Alltech CN (Alltech Associates) 0.46 × 25 cm. Preparative liquid chromatography was performed on a 10 μm silica column, 5 × 25 cm. Proton magnetic resonance spectra were recorded on a Varian HR220 (220 MHz) spectrometer. Low-resolution electron-impact mass spectra were obtained on a Finnigan-MAT 731 and gas chromatographic/mass spectra (GCMS) on a VG 7070E. Ultraviolet–visible (UV) absorption spectra were recorded on a Perkin-Elmer Model 552 spectrophotometer.

UV Analyses. The charge-transfer absorption between DPE and $TCNQF_4$ was recorded by adding at least a 10-fold excess of DPE to an air- or oxygen-saturated solution of $TCNQF_4$ (ca. 3×10^{-3} M) in acetic acid and scanning from 800 to 200 nm. Both the magnitude and the decay rate of the 575 nm absorption were found to increase with increasing DPE concentration.

Reaction Preparation. A solution of $TCNQF_4$ (2×10^{-3} to 5×10^{-3} M) in acetic acid was placed in a round-bottomed flask and magnetically stirred while purging with oxygen. DPE was added (0.1–0.2 M) and the reaction was stirred open to the air for ca. 24 h. The $TCNQF_4$ was consumed within 15 min; however, GC analysis showed that BP and HAC required several hours to be produced.

BP and HAC were isolated from the reaction mixture by HPLC and identified by comparison of retention times, ^1H NMR, and mass spectral data with authentic compounds. DPEO was shown by gas chromatography and ^1H NMR spectroscopy to be rapidly converted to HAC in acetic acid.

DPE-d_{10} Labeling. DPE-d_{10} (0.14 M) was added to a reaction mixture ca. 15 min after DPE (H_{10}) (0.14 M) had been added. The reaction solutions were analyzed 24 h after the addition of the DPE (H_{10}). The samples were diluted with acetonitrile and analyzed by GC-MS. The total ion yields at m/e 183 ($Ph_2 C^+OH$) and 193 (d_{10}) were monitored and compared to obtain the relative yield of HAC and HAC-d_{10}.

AIBN Initiated Oxidation of DPE in Acetic Acid. DPE (0.05 mL) was added to an oxygen-saturated acetic acid solution containing AIBN (2 mg, 6.7 mmol). The solution was heated at 85 °C for 30 min. Analysis by gas chromatography revealed both BP and HAC. Control experiments showed that these products are not formed in significant amount in the absence of the free radical initiator.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Registry No. DPE, 530-48-3; $TCNQF_4$, 29261-33-4.

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(10) Selikson, S. J.; Watt, D. S. *J. Org. Chem.* **1975**, *40*, 267.
(11) Rebek, J., Jr. *Heterocycles* **1981**, *15*, 517.
(12) *Org. Synth.* **1941**, *1*, 226.
(13) Wheland, R. C.; Martin, E. L. *J. Org. Chem.* **1975**, *40*, 3101.
(14) Peacock, N. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 3632.
(15) Mango, F. D.; Bonner, W. A. *J. Org. Chem.* **1964**, *29*, 1367.
(16) Eliel, E. L.; Delmonte, D. W. *J. Org. Chem.* **1956**, *21*, 596.