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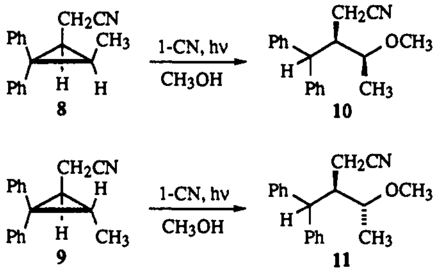
of the large rate constants for these reactions, an "early" transition state with a long nucleophile–carbon separation is expected, which should lead to diminished steric effects. However, this explanation does not rationalize why nucleophiles prefer to add at the more hindered carbon atom. Since the preferential substitution at C2 rather than C3 must be due to energy differences between the two S_N2 transition states, we hypothesize that alkyl substituents stabilize positive charge at the carbon atom undergoing substitution, thereby reversing the normal regiochemistry of substitution. The electronic effects apparently overwhelm the smaller steric effects in the three-electron S_N2 transition states. Our Hammond postulate argument for early transition state structures further suggests that the transition-state charge distributions may be similar to those of the ground-state cation radicals. EPR and CIDNP investigations on unsymmetrically substituted cyclopropane cation radicals show that the unpaired spin density (and presumably the charge distribution) is principally located in the more highly substituted cyclopropane bonds.[9] These data further support our proposed explanation.

Cyclopropanes **8** and **9** were prepared to test our electronic hypothesis.[10] Here, the substituents at C2 and C3 are comparable sterically but different electronically. Photooxidation of racemic **8** and **9** in methanol leads exclusively to formation of racemic, threo **10** and erythro **11**, respectively. Both of these products are the result of nucleophilic substitution with inversion of configuration at the carbon atom which bears the more electron-donating alkyl substituent.



In summary, three-electron S_N2 substitutions on diarylcyclopropane cation radicals by methanol are dominated by electronic rather than steric factors.[11] This leads to the surprising result that substitutions occur at the more hindered center, even when it is tertiary or neopentyl.

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(9) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6805. (b) Roth, H. D.; Schilling, M. L. M.; Schilling, F. C. *J. Am. Chem. Soc.* **1985**, *107*, 4152. (c) Qin, X.-Z.; Snow, L. D.; Williams, F. *J. Am. Chem. Soc.* **1984**, *106*, 7640. (d) Qin, X.-Z.; Williams, F. *Tetrahedron* **1986**, *42*, 6301.

(10) Prepared by the rhodium acetate catalyzed[9a,b] reaction of 1,1-diphenylpropene[9c] and ethyl diazoacetate. The cis and trans cyclopropyl esters so obtained were separated by medium-pressure column chromatography (SiO_2, 97:3 hexane/ethyl acetate). The esters were then reduced with lithium aluminum hydride in tetrahydrofuran. The resulting alcohols were converted into tosylates (tosyl chloride, pyridine, 0 °C), which were then converted into **8** and **9** by reaction with tetraethylammonium cyanide in dimethyl sulfoxide (25 °C, 8 h). (a) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695. (b) Doyle, M. P.; Dorow, R. L.; Buhro, W. E.; Griffin, J. H.; Tamblyn, W. H.; Trudell, M. L. *Organometallics* **1984**, *3*, 44. (c) Simes, B. E.; Rickborn, B.; Flournoy, J. M.; Berlman, I. B. *J. Org. Chem.* **1988**, *53*, 4613.

(11) In general, the balance between electronic and steric factors in three-electron S_N2 reactions is not yet clear. Variations in both the structure of the cation radical and the nucleophile may well provide cases where, for example, a later transition state structure (with a shorter carbon–nucleophile separation) results in steric effects large enough to overwhelm the electronic effects.

Selective Catalytic Debromination by C_{60} Mono-, Di-, and Trianion[1]

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The fullerenes have stimulated intense interest and activity with regard to their structures, properties, and reactivities.[2-6] Several reports have demonstrated hydrogenation,[7] halogenation,[8] alkylation,[9] epoxidation,[10] and recently, the dimerization of radical adducts.[11] Several voltammetric studies of C_{60} also have appeared.[7,12-21] Generally, it has been found that C_{60} will undergo stepwise reduction in solution by up to six electrons,[18] depending on the experimental conditions. The long lifetime of the anions in solution and the nearly equal spacing of the voltammetric reduction waves suggest that it should be possible to use C_{60} as a highly selective intermolecular electron transfer catalyst for a wide range of reducible species. In this communication we report rate constants for electron-transfer reactions of C_{60} anion, dianion, and trianion with a number of bromides and vicinal dibromides. The implication of these results is that a single redox catalyst can be used to carry out a selective, stepwise, multistep reduction of complex organic compounds. To our knowledge, these are the first reported examples of homogeneous redox catalysis by C_{60} anions.

Voltammetric data for C_{60}, benzoquinone (BQ), 9,10-dicyanoanthracene (DCA), and 1,4-dicyanonaphthalene (DCN) in toluene/acetonitrile (5.4:1 v/v) containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte are given in Table I. Also included are the irreversible peak potentials for the bromides used in this study. The application of homo-

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(2) Taylor, R.; Holloway, J. H.; Hope, E. G.; Avent, A. G.; Langley, G. H.; Dennis, T. J.; Hone, J. P.; Kroto, H. W.; Walton, R. M. *J. Chem. Soc., Chem. Commun.* **1992**, 665.

(3) Loy, D. A.; Assink, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 3977.

(4) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213.

(5) Dixon, D. A.; Matsuzawa, N.; Fukumaga, T.; Tebbe, F. N. *J. Phys. Chem.* **1992**, *96*, 6107.

(6) Diederich, F.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 678.

(7) Haufler, R. E.; Conceicao, J.; Chibante, L. P. E.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

(8) Selig, H.; Lishitz, C.; Peres, T.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr.; Smith, A. B., III. *J. Am. Chem. Soc.* **1991**, *113*, 5475.

(9) Bausch, J. W.; Prakash, G. K. S.; Olah, G. A.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 3205.

(10) Greegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103.

(11) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* **1992**, *114*, 5454.

(12) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

(13) Dubois, D.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6446.

(14) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

(15) Johnson, R. D.; Meijier, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983.

(16) Allemand, P. M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

(17) Li, Q.; Wudl, F.; Thilgen, C.; Whetten, R. L.; Diederich, F. *J. Am. Chem. Soc.* **1992**, *114*, 3994.

(18) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.

(19) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456.

(20) Jehoulet, C.; Obeng, Y. S.; Kim, Y. T.; Zhou, F. M.; Bard, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4237.

(21) Obeng, Y. S.; Bard, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 6299.

0002-7863/93/1515-367$04.00/0

Table I. Electrochemical Data and Rate Constants for the Reduction of Bromides and Vicinal Dibromides by C_{60} Anions

bromide[a] (E_p vs Ag/AgCl)	catalyst (oxidized form)	$E^{\circ\,a,b}$ (V vs Ag/AgCl)	$k_{ET}{}^{c}$ ($M^{-1}\,s^{-1}$)
1,2-dibromotetrachloroethane (−0.84)	C_{60}	−0.416 (59)	$2.2 \pm 0.1 \times 10^3$
	BQ	−0.359 (60)	$1.95 \pm 0.06 \times 10^2$
ethyl 2,3-dibromopropionate (−1.41)	C_{60}	−0.416 (59)	nr
	C_{60}^-	−0.836 (59)	$1.2 \pm 0.1 \times 10^4$
	DCA	−0.810 (61)	$5.9 \pm 0.1 \times 10^3$
α,α′-dibromo-*p*-xylene (−1.48)	C_{60}	−0.416 (59)	nr
	C_{60}^-	−0.836 (59)	22.8 ± 0.1
	DCA	−0.810 (61)	48.5 ± 0.1
ethyl 2-bromopropionate (−1.84)	C_{60}^-	−0.836 (59)	nr
	C_{60}^{2-}	−1.378 (61)	$8.1 \pm 2 \times 10^2$
	DCN	−1.302 (60)	$7.2 \pm 0.1 \times 10^2$
ethyl 2-bromoisobutyrate (−1.99)	C_{60}^-	−0.836 (59)	nr
	C_{60}^{2-}	−1.378 (61)	$4.5 \pm 2 \times 10^4$
	DCN	−1.302 (60)	$3.0 \pm 0.3 \times 10^3$

[a] A scan rate of 100 mV/s was used. The standard potential for ferrocene in this solvent system is 0.571 V. [b] The value of $E_p{}^a - E_p{}^c$ in millivolts is in parentheses. [c] Average of rate constants obtained from two different scan rates using three different concentrations of bromide; nr = no reaction observed with up to 10 equiv of added bromide.

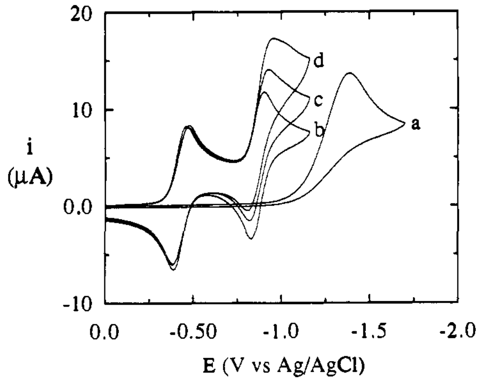

Figure 1. Voltammograms at 50 mV s^{-1} in toluene/acetonitrile (5.4:1 v/v) containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte at a glassy carbon electrode of (a) ethyl 2,3-dibromopropionate (0.6 mM), (b) C_{60} (0.6 mM), (c) C_{60} (0.6 mM) + ethyl 2,3-dibromopropionate (0.6 mM), and (d) C_{60} (0.6 mM) + ethyl 2,3-dibromopropionate (1.2 mM).

geneous redox catalysis for the determination of electron-transfer rate constants has been developed by Savéant and his co-workers.[22-24] The mechanism for the catalytic reduction of a bromide (X = H) is given by eqs 1, 2, and 3a while that for the vicinal dibromide (X = Br) is given by eqs 1, 2, 3b, and 4. In both cases a total of two electrons are transferred with both homogeneous electron-transfer reactions (eqs 2 and 3a or 4) resulting in the regeneration of the oxidized form of the catalyst. It is, in fact, the regeneration of the oxidized form of the catalyst near the electrode surface that is responsible for the observed catalytic currents (Figure 1).

$$A \rightleftarrows A^{\bullet -} \qquad (1)$$

$$A^{\bullet -} + RCHBrCH_2X \rightarrow A + RC^{\bullet}HCH_2X + Br^- \qquad (2)$$

$$A^{\bullet -} + RC^{\bullet}HCH_2X \rightarrow A + RC^{-}HCH_2X \qquad (3a)$$

$$RC^{\bullet}HCH_2X \rightarrow RCH{=}CH_2 + X^{\bullet} \qquad (3b)$$

$$A^{\bullet -} + Br^{\bullet} \rightarrow A + Br^- \qquad (4)$$

Our initial study has been to establish the efficacy of using C_{60} in its various oxidation states as a redox catalyst and to compare its reactivity in this regard with the reactivities of other aromatic radical anions. It is assumed in this treatment that the first electron transfer (eq 2) is rate limiting. In addition, digital simulation of the voltammetric waves is consistent with the assumption that the catalysts are not consumed by follow-up reactions in the case of the dibromides (Figure 1). However, a small amount of coupling between C_{60} and the alkyl radicals (or anions) is evident in the reactions of ethyl 2-bromopropionate and ethyl 2-bromoisobutyrate. The possibility of coupling of radical or anionic intermediates with the C_{60} skeleton is potentially important and may lead to a general approach to the synthesis of C_{60} adducts by preparative electrolysis. For the determination of rate constants, however, the apparent coupling is a complication that results in larger experimental errors on the rate constants in Table I. In all cases, rate constants were obtained from the appropriate working curves that were obtained by digital simulation.

It is clear from the kinetic data in Table I that the C_{60} anions are not unusually reactive (or for that matter unusually unreactive) toward the bromides used in this study. Thus, the reactivities of other organic radical anions with similar E° values (i.e., C_{60} versus BQ, C_{60}^- versus DCA, and C_{60}^{2-} versus DCN) are similar.[25] This can be understood since it has been shown, recently, that the kinetics of electron transfer to alkyl halides is determined primarily by the homolytic bond dissociation free energy of the neutral halide,[26,27] so changes in the Marcus/Hush-like solvent reorganization energies of the catalysts entail a relatively small additional contribution to the overall activation free energy for the reaction.[27]

In conclusion, this work represents the first determination of rate constants for intermolecular electron transfer reactions of C_{60} mono-, di-, and trianion. The selectivity with which the different classes of bromides and dibromides are catalytically reduced by the C_{60} anions is a result of the convenient spacing of ca. 400 mV between the successive reduction waves. This spacing represents a change in the driving force of ca. 10 kcal mol^{-1}. As a result C_{60}^- will only react with a highly electron deficient dibromide such as 1,2-dibromotetrachloroethane and does not react with either of the moderately electron deficient dibromides (Table I). Similarly, C_{60}^{2-} does not react with the *α*-bromo esters since the E° values for the dissociative reduction of these compounds are more negative than those for the vicinal dibromides. This high selectivity as a function of the electron demand of the bromide may have some potentially useful synthetic applications. A number of possibilities are currently under investigation.

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(22) Andrieux, C. P.; Dubois-Bouchait, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1980**, *113*, 19.

(23) Andrieux, C. P.; Gelis, L.; Savéant, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 786.

(24) Savéant, J. M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1.

(25) It was pointed out by a reviewer that the rate constants for the reactions of C_{60}^{2-} and C_{60}^{3-} will be underestimated because these anions will undergo comproportionation with C_{60} and C_{60}^-, respectively; i.e., $C_{60}^{n-} + C_{60}^{(n-2)-} \rightleftarrows 2C_{60}^{(n-1)-}$. The equilibrium constant for this reaction is ca. 10^7 and will have the effect of lowering the concentration of the catalyst (i.e., it is consumed faster than would be anticipated). The magnitude of this effect will depend on the overall rates of the competing processes and is more important when the reaction with the bromide is slow. However, from digital simulation, the rate constants will not be underestimated by more than 15–20%.

(26) Lexa, D.; Savéant, J. M.; Schäfer, H. J.; Su, K.; Vering, B.; Wang, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 6162.

(27) Andrieux, C. P.; Le Gorande, A.; Savéant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 6892.