

Redox Reaction of Benzyl Radicals with Aromatic Radical Ions Photogenerated. The Marcus Inverted Region and the Selective Formation of Carbocations or Carbanions

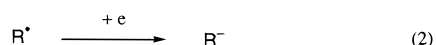
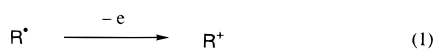
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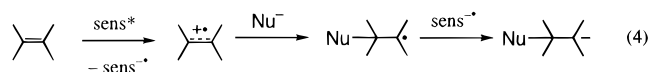
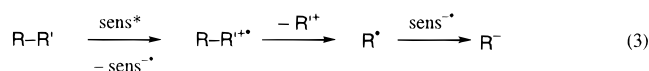
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Abstract: Efficient redox reactions of benzyl-type radicals were achieved by irradiating an aromatic donor/acceptor pair with substituted dibenzyl ketones as a radical precursor in MeOH–MeCN. In this system, the aromatic radical ion pair was generated by photoinduced electron transfer followed by one-electron oxidation and reduction of photogenerated benzyl radicals (R^{\bullet}) by the radical ions to afford benzyl cations (R^+) and anions (R^-). The cations and anions were trapped by MeOH to yield ROME and RH, respectively. The relative product ratios were determined for a variety of donor–acceptor pairs, reflecting the relative efficiencies of the redox reaction of benzyl radicals with a steady-state concentration of radical ions. The selective formation of carbocations or carbanions was achieved in some sets of donor/acceptor pairs. Assuming that the radical ions exist in a 1:1 ratio in the steady state, the product ratios are equal to the relative electron transfer rates, which are analyzed in terms of the free energy changes of the processes. The present results indicated that the rates became maximal at the energy gap of ca. -0.5 eV, representing a novel example of the Marcus inverted region. This interpretation is discussed in comparison with other related cases and in relation to recent theories on electron transfer rates.

Organic electron transfer (ET) reactions proceed mostly via an initial one-electron transfer (E) and the following reaction (C) of radical ion intermediates. When the primary products from radical ions still have an open-shell radical structure, secondary electron transfers leading to non-radical products (eqs 1 and 2) are frequently involved. Such a sequence is known as an ECE process and is very common in electrochemical reactions.¹



Redox reactions of radical species are also involved in many photosensitized ET reactions.² Typically, a back electron transfer between the radical and sensitizer radical ions, by which the sensitizer is regenerated, is involved in many photocatalytic ET processes. In the oxidative bond cleavage (eq 3)³ or in the addition of nucleophiles to olefin radical cations (eq 4),⁴ the efficiencies of the last steps are essential in determining products. In these reactions, the redox process of organic radicals (eqs 1 and 2) is of great importance and care must be taken in selecting the applied electrode potential or on the choice



of photosensitizers.⁵ However, little attention has been directed toward the secondary redox processes because of masking by the prior ET step or chemical reactions.

According to the Marcus theory,⁶ the electron-transfer rate depends on the free energy change of the process (ΔG). Especially important is that the rate reaches maximum when the energy gap ($-\Delta G$) equals the reorganization energy (λ) but decreases with increasing exothermicity when $-\Delta G > \lambda$ (the Marcus inverted region). Since electron transfers between radicals and radical ions are highly exothermic, consideration of the inverted region might be very important.

Although actual examples for the Marcus inverted region have been demonstrated recently,^{7–19} many other cases in photo-

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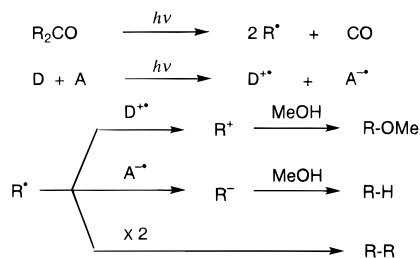
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Scheme 1



chemical processes do not show such a region, as exemplified in the well-known fluorescence quenching study by Rehm and Weller.²⁰ In such cases, formation of radical ions in the low-lying excited state has been suggested as the reason for the absence of the inverted region.²¹ In fact, in all cases showing the Marcus inverted region,^{7–19} the electron transfer occurs between radical species affording closed-shell species where excited products are unlikely to be formed. The inverted region is not commonly observed for intermolecular electron transfers, even in the ET's between radical species.^{22–24} Recently, new explanations have been proposed for the lack of the inverted region, one of which deals with a dielectric saturation effect of solvents.²⁵ According to this, the ET rate depends on the type of ET, i.e., charge separation, shift, or recombination. Another theory has pointed out the dependence of donor–acceptor distance on the reorganization energy,²⁶ in which the ET rate is essentially independent of the substrate character or the type of ET. Thus, the systematic study of the electron transfer of radical species is interesting and crucial for the consideration of such theories.

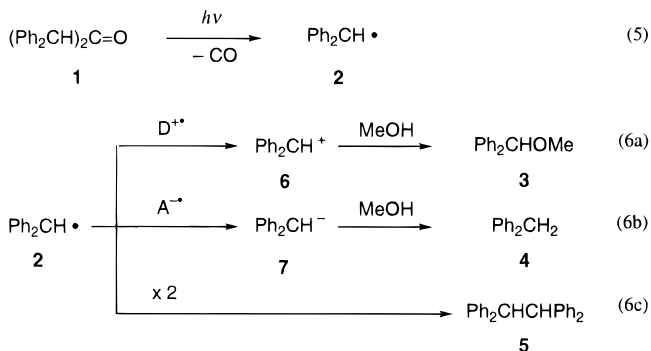
Recent development of the photomodulation voltammogram allows the precise determination of redox potentials for various radical intermediates.²⁷ However, the direct observation of such redox reactions of radicals with various oxidants and reductants is quite difficult because of involvement of unstable species of short lifetimes. Then, in order to study the ET of radicals with aromatic radical ions, we have examined a redox system as shown in Scheme 1. If photogenerated radical ions are stable enough so that the radical cation/anion pair exists as free ions in a 1:1 ratio during the irradiation, only a back electron transfer

takes place without any chemical reactions. In such a case, simultaneous generation of a transient radical (R^{\bullet}) may bring about its redox reaction with the radical ions, leading to the formation of the corresponding carbenium ion ($R^{+\bullet}$) and carbanion ($R^{-\bullet}$). In the presence of MeOH, the cation and anion are trapped by MeOH affording ROME and RH, respectively, the ratio of which may reflect the relative rate for the electron transfer. We have employed diphenylmethyl and substituted benzyl radicals, since they are stable enough to give the corresponding coupling products in high yields²⁸ and their redox potentials are already known.²⁷ The dibenzyl ketones seem to be suitable as the precursor, since the photocleavage leading to two benzyl radicals proceeds quite efficiently ($\Phi \approx 0.7$) and nonsymmetrical dibenzyl ketones affords a statistical mixture of coupling products, indicating that truly “free” radicals are generated.²⁹ If appropriate amounts of $D^{+\bullet}$ and $A^{-\bullet}$ are generated by adjusting initial concentrations of donor D and acceptor A, the photochemical formation of oxidant and reductant ions may be achieved.³⁰

We wish to report here the results on the simultaneous irradiation of donor, acceptor, and ketone. The redox reaction of radicals with aromatic radical ions has been investigated from the product ratios of ROME/RH for a various combination of radical/donor/acceptor. The selective formation of carbocations and carbanions was achieved in some sets of donor/acceptor pairs, and the relative rates were discussed on the basis of the Marcus theory.

Results and Discussion

Products of the Co-irradiation of *sym*-Tetraphenylacetone, Naphthalene, and *p*-Dicyanobenzene. The irradiation of *sym*-tetraphenylacetone (**1**) is known to generate effectively diphenylmethyl radical **2** (eq 5), affording 1,1,2,2-tetraphenylethane (**5**) as the radical-coupling product in high yield. However, the irradiation (>290 nm) of 0.3 mM **1** in MeOH–MeCN (1:9) in the presence of 10.0 mM each of naphthalene (N) and *p*-dicyanobenzene (DCB) under Ar for 2 h resulted in the formation of diphenylmethyl methyl ether (**3**) and diphenylmethane (**4**) in 3.3 and 49% yields, respectively, in addition to a 22% yield of **5**. In this system, naphthalene ($E_{1/2}^{\text{ox}} = +1.80$ V vs SCE)^{11d} also absorbs light^{31a} and its fluorescence is quenched by DCB ($E_{1/2}^{\text{red}} = -1.60$ V vs SCE)² yielding the corresponding radical ions $N^{+\bullet}$ and $DCB^{\bullet-}$.^{31b} The formation of **3** and **4** suggests the one-electron oxidation and reduction of **2** ($E_{1/2}^{\text{ox}} = +0.35$ V and $E_{1/2}^{\text{red}} = -1.14$ V vs SCE)^{27a} to yield carbenium ion **6** and carbanion **7** as shown in eq 6.



When the concentration of **1** was increased up to 1.0 mM, the yield of dimer **5** increased (32%) and those of **3** and **4**

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decreased (1.9% and 41%, respectively), as the steady state concentrations of radical ions may be decreased. However, the product ratios **3/4** were almost unchanged (i.e., 0.06 ± 0.02), indicating the constant relative efficiency for the ET processes of **2** (eqs 6a and 6b). The free energy changes (ΔG) in the electron transfer of radical R^{\bullet} can be calculated from eqs 7 and 8 for the oxidation of **2** by $N^{\bullet+}$ and for the reduction by $DCB^{\bullet-}$, respectively; for the case of **2**, the oxidation ($-\Delta G_{ox} = 1.45$ eV) is much more exothermic than the reduction ($-\Delta G_{red} = 0.46$ eV). Thus, the observation of predominant reduction of **2** was quite striking.

$$\Delta G_{ox} = E_{1/2}^{ox}(R^{\bullet}) - E_{1/2}^{red}(D^{\bullet+}) = E_{1/2}^{ox}(R^{\bullet}) - E_{1/2}^{ox}(D) \quad (7)$$

$$\Delta G_{red} = E_{1/2}^{ox}(A^{\bullet-}) - E_{1/2}^{red}(R^{\bullet}) = E_{1/2}^{red}(A) - E_{1/2}^{red}(R^{\bullet}) \quad (8)$$

When a substituted naphthalene such as 2-methylnaphthalene (MN, $E_{1/2}^{ox} = +1.68$ V vs SCE)^{11d} or 2,6-dimethylnaphthalene (DMN, $E_{1/2}^{ox} = +1.59$ V vs SCE)^{11d} was employed, the yields of **3**, **4**, and **5** for 1 mM **1** were 13%, 52%, and 12% for MN and 21%, 43%, and 20% for DMN, respectively. The product ratios of **3/4**, averaged for the reaction with 1.0 to 5.0 mM **1**, increased up to 0.41 ± 0.17 for MN and 0.51 ± 0.02 for DMN. If the ratios were directly related to the ET rates, the more efficient oxidation of **2** by naphthalene radical cations with decreasing oxidation potentials may be indicative of the Marcus inverted region.

The redox reaction of radical **2** was supported by the following facts:

(i) The irradiation of N and DCB in the absence of **1** in MeOH–MeCN for 2 h afforded practically no products, the recoveries of N and DCB being more than 98%. This may lead to an assumption that the radical ions $N^{\bullet+}$ and $DCB^{\bullet-}$ are long-lived and stable until they react by the back ET between them.³² By prolonged irradiation for 30 h, both N and DCB were slightly consumed (ca. 5%), and a trace amount of 1-methoxynaphthalene was detected by GC-MS as a product, which was not found among byproducts in the co-photolysis of **1**, N, and DCB.

(ii) The irradiation of **1** in the absence of either N or DCB did not yield **3** and **4** at all and dimer **5** was obtained in more than 90% yield. This indicates that the radical **2** is unreactive toward N, DCB, and MeOH, consistent with the well-known inertness of benzyl-type radicals toward C–H bonds.³³

(iii) When the solution was irradiated in 5% CH₃OD (99.5 atom % D), monodeuterated **4** (i.e., Ph₂CHD) was obtained with 95.7% isotopic purity, indicating clearly that **4** was formed by the protonation of carbanion **7**, not by the hydrogen abstraction of **2**.

(31) (a) Since the extinction coefficients of **1** and N at 313 nm are 220 and 90, respectively, about 30% of light is absorbed by N. The quantum yields for the formation of $D^{\bullet+}$ and $A^{\bullet-}$, however, are governed by the back electron transfer and we have no information about the true yields for free ions for various D–A pairs in the tables. (b) Grellmann, K. L.; Watkins, A. R.; Weller, A. *J. Phys. Chem.* **1972**, *76*, 469.

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Table 1. Redox Potentials of Ketones and Radicals

R	R ₂ C=O (V vs SCE) ^a		R [•] (V vs SCE)	
	$E_{1/2}^{ox}$	$E_{1/2}^{red}$	$E_{1/2}^{ox}$	$E_{1/2}^{red}$
(C ₆ H ₅) ₂ CH	~+2.3	<–2.2	+0.35 ^b	–1.14 ^b
4-ClC ₆ H ₄ CH ₂	~+2.4	<–2.2	+0.80 ^c	–1.40 ^c
C ₆ H ₅ CH ₂	+2.29	<–2.2	+0.73 ^c	–1.43 ^c
4-MeC ₆ H ₄ CH ₂	~+2.2	<–2.2	+0.51 ^c	–1.62 ^c
4-MeOC ₆ H ₄ CH ₂	+1.59	<–2.2	+0.26 ^c	–1.82 ^c

^a Obtained by rotating ring-disk electrode voltammetry (see Experimental Section). ^b Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132. ^c Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635.

(iv) Benzyl-type cations^{34ab} and anions^{34c} have been known to react with MeOH quite rapidly, the rate constants being $6\text{--}8 \times 10^7$ and ca. 2×10^8 M⁻¹ s⁻¹, respectively. Thus, in the presence of >5% MeOH, the two ions react with MeOH within 10 ns, much faster than any other reactions with transient species. If a part of $N^{\bullet+}$ is decomposed by the reaction with MeOH, a decrease of cation formation is expected at higher MeOH concentration. This is not the case, because the product ratios were practically not affected by the amount of methanol in the range from 5% to 20%. In contrast, at <1% methanol, the ratio of **3/4** was decreased down to <0.03, and irradiation in the absence of MeOH afforded **4** and a small amount of benzophenone, which might be formed by reaction of **6** with trace water followed by oxidation. The product ratios at the lower MeOH concentration were not reproducible, probably because of the variable amount of contaminating water. Thus, while the electron transfer may be independent of methanol, a substantial amount of methanol is required for the efficient trapping of cation **6**.

(v) Since the fluorescence of N is unaffected by the addition of ketone **1** but efficiently quenched by DCB **1** at nearly diffusion controlled rate, $k_q = 1.8 \times 10^{10}$ M⁻¹ s⁻¹,³⁵ the excited singlet state of N undergoes exclusively ET with DCB. Under these conditions, DCB slightly absorbs light, but irradiation of **1** and DCB does not yield **3** or **4**. Moreover, the redox potential of **1** ($E_{1/2}^{ox} = \sim +2.3$ V and $E_{1/2}^{red} < -2.2$ V vs SCE)³⁶ indicates that the electron transfer of **1** with $N^{\bullet+}$ or $DCB^{\bullet-}$ is energetically unfavorable. Thus, the direct electron transfer of ketone **1** is not involved.

(vi) Other transient species involved here are the excited state ketone and an acyl radical (Ph₂CH–CO[•]). Although the lifetime of the singlet excited state of **1** is not known, dibenzyl ketone has only a few nanoseconds fluorescence lifetime.³⁷ The triplet state instantaneously undergoes the C–C bond cleavage generating benzyl and phenacetyl radicals, and the latter radical immediately affords another molecule of benzyl radical by decarbonylation.³⁸ The acyl radical (Ph₂CH–CO[•]) has been known to have a lifetime as short as ~ 8 ns.²⁸ Thus, such transients are quite short lived and their intermolecular reactions can be eliminated.

(vii) As the alkylation of aromatic nitriles is known in photoinduced ET reactions,³⁹ a radical–radical ion combination

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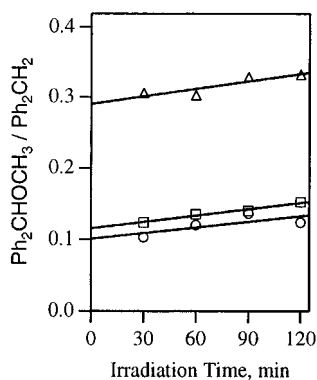
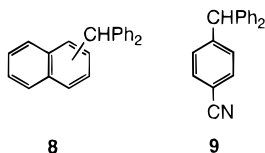


Figure 1. Product ratios of $\text{Ph}_2\text{CHOCH}_3/\text{Ph}_2\text{CH}_2$ on the irradiation of 1.5 mM **1**, 10 mM DCB, and 10 mM naphthalenes: naphthalene (circle), 2-methylnaphthalene (square), or 2,6-dimethylnaphthalene (triangle), in 5% MeOH–MeCN.

may lead to a coupling reaction rather than the electron transfer. In the present case, such a reaction seems not to be a major pathway, since the total yield of **3**, **4**, and **5** was usually as high as 70–80% and the recoveries of N and DCB were more than 95%. Possible coupling products are adducts of radicals and sensitizers (e.g., **8** and **9**), only trace amounts (<1%) of which



were detected among the byproducts by GC-MS analyses. The reported DCB-sensitized fragmentation of **5** (cf. eq 3, $R = R' = \text{Ph}_2\text{CH}$) in MeOH–MeCN afforded **3** and **4** in a 1:1 ratio,^{3b} indicating that the reaction between **2** and $\text{DCB}^{\bullet-}$ yields **7** quantitatively. While the reaction of **2** with $\text{N}^{\bullet+}$ has never been examined, similar electron transfer of Me- or MeO-substituted naphthalene radical cations with 1,1-diphenylethyl⁴⁰ or bis(4-methoxyphenyl)methyl radicals⁴¹ has been suggested to proceed efficiently. Thus, the coupling reaction of radicals with radical ions is not involved in the present system.

(viii) The observation of less efficient oxidation of radical **2** by $\text{N}^{\bullet+}$ may be due to the formation of a side product that is lower in oxidation potential than naphthalene or **2**. If such a product is formed, a secondary electron transfer will occur between $\text{N}^{\bullet+}$ and the byproduct with formation of its radical cation, which cannot oxidize **2**. In fact, the product ratio of **3/4** changed during the progress of irradiation, probably due to some effect of byproducts. Therefore, the product ratios at zero irradiation time which could be determined by extrapolation of the values at the initial stage of photoreaction should be more reliable (Figure 1). The resulting ratios of **3/4** were 0.10 ± 0.01 , 0.12 ± 0.01 , and 0.29 ± 0.01 with N, NM, and DMN, respectively, which again indicated that the oxidation of **2** became more efficient with decreasing exothermicity. Repeated experiments showed that the selectivities were reproducible within $\pm 30\%$.

(ix) In the presence of nucleophiles such as alcohols, aromatic radical cations may be in reversible equilibrium with the alcohol adducts.⁴² Therefore, the effect of alcohols was examined. With 5% MeOH, EtOH, *i*-PrOH, and *t*-BuOH, the product ratios extrapolated to initial time were almost constant, i.e., **3/4** =

0.10 ± 0.01 , 0.10 ± 0.01 , 0.08 ± 0.01 , and 0.10 ± 0.01 , respectively. This is another piece of evidence against the formation of alcohol adducts.

(x) Dimer formation of aromatic radical ions may affect the ET rates, as in the reported case of ET between naphthalene dimer radical cation and 9,10-dicyanoanthracene radical anion ($\text{DCA}^{\bullet-}$) which is faster than that in the solvent-separated ion pair of monomer and $\text{DCA}^{\bullet-}$.⁴³ The laser flash photolysis study has shown that a small portion of $\text{N}^{\bullet+}$ exists as the dimer radical cation at ca. 10 mM naphthalene.³⁵ In the present case, however, the contribution of dimer formation cannot account for the slower ET for $\text{N}^{\bullet+}$, since the extrapolated product ratios are not affected by the naphthalene concentrations, i.e., **3/4** = 0.18 ± 0.01 , 0.13 ± 0.01 , and 0.12 ± 0.02 at 5, 10, and 20 mM naphthalene, respectively.

Thus, all the facts described above suggest that the efficient electron transfer between radical **2** and radical ions is achieved in the present co-irradiated system, the reduction of **2** by DCB anion radical being more efficient than the oxidation by naphthalene radical cations.

The Free Energy Change (ΔG) Dependence on the Redox Reaction of **2.** In order to examine the free energy gap dependence on the ET rates, the relative efficiencies were determined for a variety of donors and acceptors as listed in Chart 1. Since it has been suggested that the electron transfer rates between aromatic radical ion pairs depend on ring-size,¹¹ donors and acceptors are classified as one-, two-, and three-ring systems.

The relative efficiencies for the oxidation of **2** with donor radical cation vs the reduction with DCB anion radical were obtained from the extrapolated product ratios of **3/4**, as summarized in Table 2 (runs 1–19). Those for the reduction with substituted dicyanobenzenes, 2,5-dimethyl-1,4-dicyanobenzene (DMDCB, $E_{1/2}^{\text{red}} = -1.75$ V vs SCE) or dicyanodurene (TeMDCB, $E_{1/2}^{\text{red}} = -1.90$ V vs SCE), were also determined with 1,3,5-trimethoxybenzene (135TrMOB) or 1,2-dimethoxybenzene (12DMOB) as reference donors. The resulting relative rates were independent of the reference (Table 2, runs 20–23) and were smaller than that for DCB, i.e., 0.30 for DMDCB and 0.35 for TeMDCB.

As shown in Figure 2, plots of the relative rates vs $-\Delta G$ were rather scattered but seemed to be curved downward on going more exothermic. When the theoretical curve was calculated from the recent formulation of electron transfer theory (eq 9) with suggested values for a vibrational reorganization

$$k_{\text{et}} = (4\pi^3/h^2\lambda_s k_b T)^{1/2} |V|^2 \sum_{w=0}^{\infty} (e^{-S} S^w/w!) \exp\{-[(\lambda_s + \Delta G + wh\nu)^2/4\lambda_s k_b T]\} \quad (9)$$

$$S = \lambda_v/h\nu$$

energy (λ_v) of 0.25 eV and an averaged frequency (ν) of 1500 cm^{-1} ,^{9b,11d} an appropriate value for the solvent reorganization energy (λ_s) was evaluated to be ca. 0.65 eV. This value is significantly smaller than those for the return ET in geminate radical ion pairs from the quenching of excited sensitizers (e.g., 1.5–2.0 eV),^{11–15} but is rather close to reorganization energies for self-exchanging reactions of organic radical ions (e.g., 0.3–0.6 eV)⁴⁴ and for ET rates within contact radical pairs (i.e., 0.5,^{19a} 0.2,^{19b} and 0.55 eV¹⁶).

The ΔG dependence was confirmed by the following experiments:

(43) Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4814.

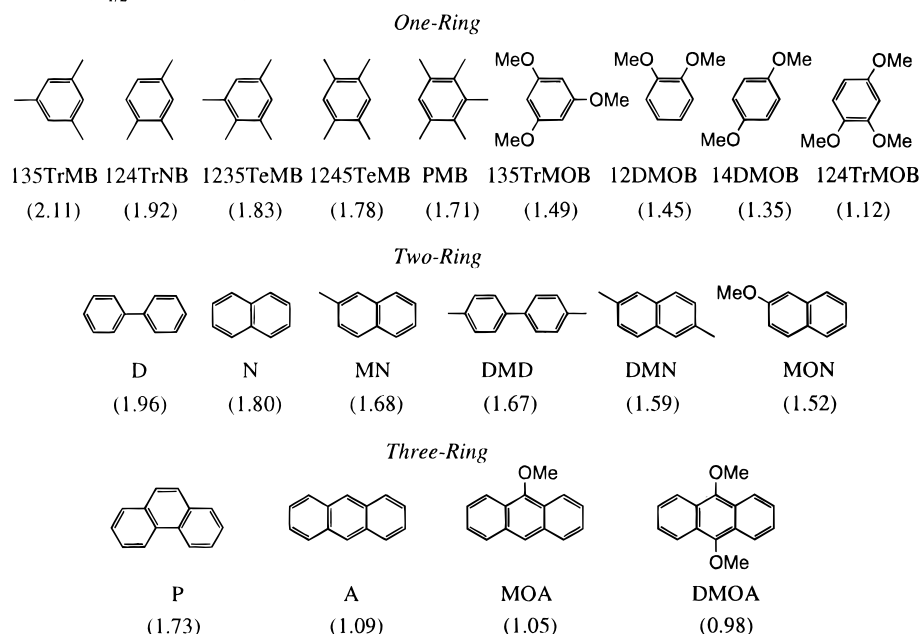
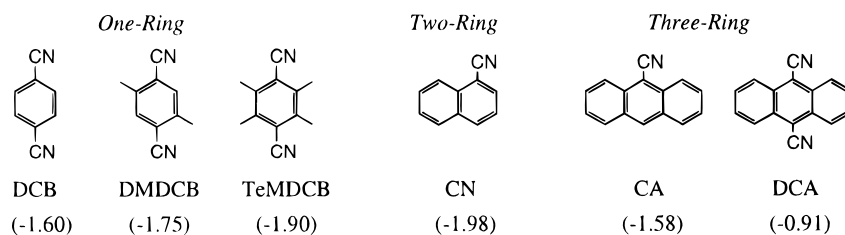
(44) See ref 6c, p 79.

(40) Arnold, D. R.; Maroulis, A. *J. Am. Chem. Soc.* **1977**, *99*, 7355.

(41) Johnston, L. J.; Kanigan, T. *J. Am. Chem. Soc.* **1990**, *112*, 1271.

(42) (a) Sehested, K.; Corfitzen, H.; Christiansen, H. C.; Hart, E. *J. J. Phys. Chem.* **1975**, *79*, 310. (b) Sehested, K.; Holcman, J.; Hart, E. *J. J. Phys. Chem.* **1977**, *81*, 1363.

Chart 1

Donors ($E_{1/2}^{\text{ox}}$, V vs SCE)Acceptors ($E_{1/2}^{\text{red}}$, V vs SCE)

(i) When donors such as 1235TeMB, 14DMOB, and D were irradiated in the presence of DCB in MeOH–MeCN for 2 h, practically no reaction took place and more than 98% of donors were recovered. The irradiation of **1** and methylated donors such as 135TrMB, 1245TeMB, and 14DMOB in the absence of DCB did not afford **3** and **4**, the dimer **5** being obtained in more than 90% yield. Since substituted benzenes and diphenyls (runs 1–10 and 13) have only weak absorption at >290 nm, DCB may also absorb light and oxidize **1** in such cases. However, the yield of dimer **5** was not affected by the addition of DCB. Thus, side reactions such as decomposition of donor

radical cations, H-abstraction of radical **2** from donors, and direct oxidation of **1** by excited DCB could be eliminated.

(ii) In the presence of a second donor (D_2), the oxidation potential of which is lower than primary donor (D_1), the second electron transfer from D_2 to D_1^{*+} will occur to yield D_2^{*+} . Since the second charge-shift reaction is expected to be as fast as the diffusion controlled rate when the difference between oxidation potentials of D_1 and D_2 is more than 0.4 V,^{11d,45} the concentration of D_2 can be kept low enough so that it does not affect the primary ET between D_1 and A. Therefore, the addition of a relatively low concentration of D_2 is expected to change the product ratio for D_1/A to that for D_2/A . This was examined for naphthalene (N), mesitylene (135TrMB), and 1,2,3,5-tetramethylbenzene (1235TeMB) as D_1 and 1,4-dimethoxybenzene (14DMOB) and 1,2,4-trimethoxybenzene (124TrMOB) as D_2 . As summarized in Table 3, the product ratio gradually shifted to that for D_2/A by the addition of D_2 , and it was found that ca. 0.5 mM of D_2 was sufficient to change the redox couple.

(iii) It has been shown that the rates of return electron transfer in solvent-separated ion pairs decrease by introducing bulky substituents such as *tert*-butyl by a factor of 2–4.⁴⁶ Therefore, steric effect on the redox reaction was examined using 1,3,5-tri-*tert*-butylbenzene (1,3,5-*t*-Bu₃B). Since the oxidation potential of 1,3,5-*t*-Bu₃B ($E_{1/2}^{\text{ox}} = 2.01$ V vs SCE)⁴⁶ is intermediate between 135TrMB ($E_{1/2}^{\text{ox}} = 2.11$ V vs SCE)^{11d} and 124TrMB ($E_{1/2}^{\text{ox}} = 1.92$ V vs SCE),^{11d} the expected relative rate may be ca. 0.2. However, a considerably lower value of 0.011 ± 0.02

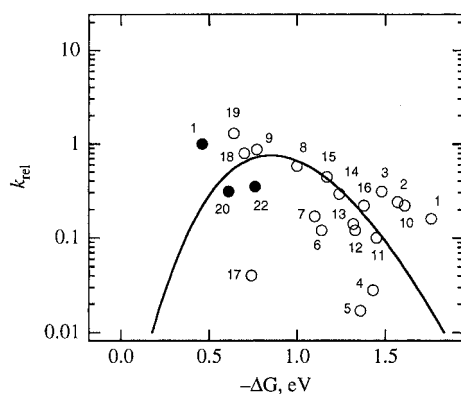


Figure 2. Plots of relative ET rates (k_{rel}) vs free energy change ($-\Delta G$) between diphenylmethyl radical and aromatic radical cations (open circle) or radical anions of 1,4-dicyanobenzenes (filled circle). The numbers denote the run number in Table 2. The curve is calculated by using the values in the text.

(45) Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055.

(46) Gould, I. R.; Farid, S. *J. Phys. Chem.* **1993**, *97*, 13067.

Table 2. Product Ratios on the Co-irradiation of **1** and Donor–Acceptor Systems^a

run no.	D ^b	−ΔG _{ox} (eV) ^c	A ^d	−ΔG _{red} (eV) ^e	3/4 ^f	k _{rel} ^g	
						ox	red
1	135TrMB	1.76	DCB	0.46	0.16 ± 0.01	0.16	(1.0)
2	124TrMB	1.57			0.24 ± 0.03	0.24	
3	1235TeMB	1.48			0.31 ± 0.03	0.31	
4	1245TeMB	1.43			0.028 ± 0.001	0.028	
5	PMB	1.36			0.017 ± 0.001	0.017	
6	135TrMOB	1.14			0.12 ± 0.01	0.12	
7	12DMOB	1.10			0.17 ± 0.01	0.17	
8	14DMOB	1.00			0.58 ± 0.02	0.58	
9	124TrMOB	0.77			0.87 ± 0.01	0.87	
10	D	1.61			0.22 ± 0.05	0.22	
11	N	1.45			0.10 ± 0.01	0.10	
12	MN	1.33			0.12 ± 0.01	0.12	
13	DMD	1.32			0.14 ± 0.01	0.14	
14	DMN	1.24			0.29 ± 0.01	0.29	
15	MON	1.17			0.44 ± 0.01	0.44	
16	P	1.38			0.22 ± 0.01	0.22	
17	A	0.74			0.040 ± 0.004	0.040	
18	MOA	0.70			0.80 ± 0.03	0.80	
19	DMOA	0.64			1.30 ± 0.12	1.30	
20	135TrMOB	1.14	DMDCB	0.61	0.37 ± 0.01	0.12 ^h	0.31
21	12DMOB	1.10			0.63 ± 0.03	0.17 ⁱ	0.28
22	135TrMOB	1.14	TeMDCB	0.76	0.33 ± 0.01	0.12 ^h	0.35
23	12DMOB	1.10			0.50 ± 0.01	0.17 ⁱ	0.35

^a A solution of 1.5 mM **1**, donor, and acceptor in 5% MeOH–MeCN was irradiated (>290 nm) for 30–120 min under argon at 20 ± 3 °C. ^b Donors, 10 mM except for P, A, MOA, and DMOA (0.5 mM); abbreviations are shown in Chart 1. ^c The free energy change on the electron transfer from **2** to donor radical cation as calculated by eq 7. ^d Substituted dicyanobenzenes (Chart 1), 10 mM. ^e The free energy change on the electron transfer from **2** to acceptor radical anion as calculated by eq 8. ^f Relative ET rates determined by extrapolation of the product ratios of **3/4** to zero irradiation time. ^g The relative rates for electron transfer of **2** as compared with that for the reduction by DCB^{•−}; ox, the oxidation by donor radical cation; red, the reduction by acceptor radical anion. ^h Excerpted from run 6. ⁱ Excerpted from run 7.

Table 3. Effect of Second Donor, D₂^a

D ₁ ^b	[D ₁] (mM)	D ₂ ^c	[D ₂] (mM)	3/4 ^d
N	10	14DMOB		0.10 ± 0.01
	10		0.005	0.12 ± 0.01
	10		0.05	0.66 ± 0.01
	10		0.5	0.88 ± 0.01
	10		10	0.58 ± 0.02
135TrMB	10	124TrMOB		0.16 ± 0.01
	10		0.001	0.11 ± 0.01
	10		0.01	0.21 ± 0.01
	10		0.1	0.44 ± 0.02
	10		0.5	0.82 ± 0.01
135TrMB	10	14DMOB	10	0.87 ± 0.01
	10		0.5	0.16 ± 0.01
	10		10	0.63 ± 0.04
1235TeMB	10	124TrMOB	10	0.58 ± 0.02
	10		0.5	0.31 ± 0.03
	10		10	0.78 ± 0.01
			10	0.87 ± 0.01

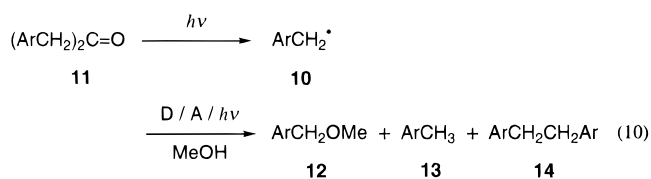
^a A solution of donors, 1.5 mM (Ph₂CH)₂CO, and 10 mM DCB in 5% MeOH–MeCN, was irradiated (>290 nm) for 30–120 min under argon at 20 ± 3 °C. ^b Primary donor: N = naphthalene; 135TrMB = 1,3,5-trimethylbenzene; 1235TeMB = 1,2,3,5-tetramethylbenzene. ^c Second donor: 14DMOB = 1,4-dimethoxybenzene; 124TrMOB = 1,2,4-trimethoxybenzene. ^d Relative ET rates for the oxidation of **2** determined by extrapolation of the product ratios of **3/4** to zero irradiation time.

was obtained, indicating that the efficiency of electron transfer decreases by a factor of ca. 20. The larger steric effect on the present ET than the reported one in solvent-separated ion pairs may suggest that the ET occurs at a closer distance, i.e., in contact ion pair.

Products from Substituted Benzyl Radicals. In order to look into a wider range of ΔG, the examination was extended to substituted benzyl radicals, *p*-X-C₆H₄CH₂• (**10**, X = H, Me, MeO, and Cl), with various redox potentials depending on the substituents (Table 1).^{27b} For the methyl- and methoxy-substituted cases which have relatively low oxidation potentials

(Table 1), care must be taken to avoid the intervention of direct reaction of the starting ketones. Thus, the donors were selected so that the electron transfer between the ketone and the donor radical cation was at least 0.2 eV endothermic.

In a similar way as the case of **1**, relative ET efficiencies of benzyl radicals (ArCH₂•; Ar = *p*-X-C₆H₄) were examined with substituted dibenzyl ketones, **11**, (ArCH₂)₂C=O, and donor/acceptor pairs as listed in Chart 1. For the semiquantitative purpose, the ratios of the corresponding benzyl methyl ethers (**11**) and toluenes (**12**) were determined at only one irradiation time and listed in Table 4. The listed values reflect the relative ET rates of benzyl radicals (ArCH₂•) since the formation of adducts of benzyl radicals and sensitizers was not significant and the resulting ratios of **12/13** did not differ largely with the irradiation time.



The present method allows the direct comparison for oxidations of a benzyl radical with various radical cations by employing the same acceptor and radical precursor, and the comparison for the reduction with different anion radicals can be made similarly. However, the relative efficiencies for different benzyl radicals cannot be evaluated directly. Then, sets of radical–radical cation combinations with almost the same −ΔG values were assumed to have identical ET rates and were employed as the references. Taking into account the ring-size effect, the rates of the following three sets were selected: (i) *p*-chlorobenzyl vs diphenyl (run 7, −ΔG = 1.16 eV), *p*-methylbenzyl vs 4,4′-dimethyldiphenyl (run 28, −ΔG = 1.16 eV), and *p*-methylbenzyl vs 2-methylnaphthalene (run 33, −ΔG

Table 4. Products on the Co-irradiation of **11** and Donor–Acceptor Systems^a

run no.	X	D ^b	[D] (mM)	−ΔG _{ox} (eV) ^c	A ^d	[A] (mM)	−ΔG _{red} (eV) ^c	conv (%) ^e	selectivity (%) ^f			k _{rel} ^g		
									12	13	14	12/13	ox	red
1	Cl	135TrMB	10	1.31	CN	15	0.58	9	4.1	1.6	80	2.6	2.6	(1.0)
2		1235TeMB	10	1.03				51	22	7.2	39	3.1	3.1	
3		1245TeMB	10	0.98				41	5.1	0.7	81	7.3	7.3	
4		12DMOB	10	0.65				3	55	26	12	2.1	2.1	
5		14DMOB	10	0.54				3	40	7.3	<4	5.5	5.5	
6		124TrMOB	10	0.32				7	55	12	6	4.6	4.6	
7		D	50	1.16				3	4.5	26	51	0.17	0.17	
8		DMD	50	0.87				3	12	3.5	27	3.4	3.4	
9		P	0.5	0.93				12	3.4	57	19	0.060	0.060	
10		A	0.5	0.29				3	10	20	42	0.50	0.50	
11		MOA	0.5	0.18				4	7.5	23	55	0.33	0.33	
12		D	50	1.16	CA	0.5	0.18	38	2.6	2.8	90	0.93	0.17 ⁱ	0.19
13		DMD	50	0.87				68	43	2.1	51	20	3.4 ^j	0.17
14		D	50	1.16	DCA	0.5	−0.49	70	4.4	1.6	93	2.8	0.17 ⁱ	0.063
15		DMD	50	0.87				42	14	<0.3	80	>50	3.4 ^j	<0.07
16	H	N	10	1.07	DCB	10	0.17	55	1.0	13	53	0.077	0.90	
17		MN	10	0.95				37	2.9	11	50	0.26	3.1	
18		DMN	10	0.86				22	3.5	12	43	0.29	3.4 ^j	12
19	Me	124TrMB	10	1.41	CN	15	0.36	<i>h</i>		(5:10:85)		0.50	0.63	
20		1235TeMB	10	1.32				<i>h</i>		(55:31:14)		1.8	2.3	
21		1245TeMB	10	1.27				<i>h</i>		(46:15:39)		3.1	3.9	
22		PMB	10	1.20				<i>h</i>		(42:13:45)		3.2	4.1	
23		135TrMOB	10	0.98				<i>h</i>		(68:32: <i>h</i>)		2.1	2.7	
24		12DMOB	10	0.94				27	58	7.7	36	7.5	9.6	
25		14DMOB	10	0.84				27	49	10	39	4.9	6.2	
26		124TrMOB	10	0.81				19	71	12	1	5.9	7.5	
27		D	50	1.45				3	2.0	19	8	0.11	0.13	
28		DMD	50	1.16				<i>h</i>		(12:88: <i>h</i>)		0.14	0.17 ⁱ	1.3
29		A	0.5	0.58				66	2.9	66	5	0.044	0.056	
30		MOA	0.5	0.54				<i>h</i>		(33:67: <i>h</i>)		0.49	0.63	
31		DMOA	0.5	0.47				<i>h</i>		(27:73: <i>h</i>)		0.37	0.47	
32		N	10	1.29	DCB	10	−0.02	40	11	15	69	0.73	0.13	
33		MN	10	1.17				32	14	14	44	1.0	0.17 ⁱ	0.17
34		DMN	10	1.08				28	16	12	46	1.3	0.23	
35		MON	10	1.01				29	9.9	21	49	0.47	0.082	
36		N	10	1.29	DMDCB	10	0.13	39	<3.0	44	18	<0.07		
37		MN	10	1.17				33	<1.7	39	17	<0.04		
38		DMN	10	1.08				45	3.2	32	36	0.10	0.23	2.3
39	MeO	135TrMOB	10	1.23	CN	15	0.16	27	65	22	8	3.0	1.3	
40		12DMOB	10	1.19				27	73	7.9	3	9.2	4.1 ^k	0.44
41		14DMOB	10	1.09				20	63	5.0	8	13	5.6	
42		124TrMOB	10	0.89				36	84	6.5	5	13	5.7	
43		A	0.5	0.83				53	15	70	8	0.21	0.10	
44		MOA	0.5	0.79				37	29	52	9	0.56	0.25	
45		DMOA	0.5	0.72				36	29	48	11	0.60	0.27	

^a A solution of 3.0 mM (*p*-X-C₆H₄(CH₂)₂CO (**11**), donor, and acceptor in 5% MeOH–MeCN was irradiated (>290 nm) for 90–120 min under argon at 20 ± 3 °C. ^b Donors: abbreviations are shown in Chart 1. ^c The free energy change on the electron transfer between benzyl radicals and radical ions as calculated by eq 7 or 8. ^d Acceptors: abbreviations are shown in Chart 1. ^e Conversion of **11**. ^f The product selectivities based on **11** reacted; the values in parentheses are product ratios. ^g The relative rates of electron transfer of benzyls with radical ions as compared with that for the reduction of *p*-Cl-C₆H₄CH₂[•] by DCB^{•−}; ox, the oxidation by donor radical cation; red, the reduction by acceptor radical anion. ^h Not determined. ⁱ Excerpted from run 7. ^j Excerpted from run 8. ^k Excerpted from run 22.

= 1.17 eV), (ii) *p*-chlorobenzyl vs 4,4′-dimethyldiphenyl (run 8, −ΔG = 0.87 eV) and benzyl vs 2,6-dimethylnaphthalene (run 18, −ΔG = 0.86 eV), and (iii) *p*-methylbenzyl vs pentamethylbenzene (run 22, −ΔG = 1.20 eV) and *p*-methoxybenzyl vs 1,2-dimethoxybenzene (run 40, −ΔG = 1.19 eV). The relative ET rates for benzyl radicals were calculated and are listed in the last two columns in Table 4.

Despite such an arbitrary assumption, the plots of relative ET rates vs ΔG clearly showed the Marcus inverted region again as shown in Figure 3. The redox reaction seems to be more efficient with the smaller-ring system, showing different curves in terms of one-, two-, and three-ring donors/acceptors. The fitting of the data with the theoretical curve (eq 9), with accepted values of λ_v = 0.25 eV and ν = 1500 cm^{−1},^{9b,11d} led to an evaluation of the solvent reorganization energies (λ_s) of 0.41, 0.37, and 0.24 eV for one-, two-, and three-ring systems, respectively. The electronic coupling elements (*V*) were not

calculated since the absolute rate constants could not be determined, but the relative values could be estimated, i.e., 1:0.38:0.23 for one-, two-, and three-ring systems, respectively. The higher λ_s and *V* values for smaller ring systems reflect a more condensed and hence more effective charge density. This tendency is qualitatively consistent with the reported result for return ET within geminate radical ion pairs.^{11b,e}

“Rehm–Weller” Behavior vs “Marcus” Behavior. All the results indicated that efficient redox reactions of radicals with aromatic radical ions were achieved by the co-irradiation of donor, acceptor, and ketone. The product ratios of ROME/RH indicate the relative efficiency of the oxidation vs the reduction with a steady-state concentration of the two radical ions. The product ratios of ROME/RH for various donor–acceptor pairs generally decreased with increasing oxidation potentials. Since the two radical ions, D^{•+} and A^{•−}, are produced in a 1:1 ratio, the product ratios reflect the relative rates for the redox reaction,

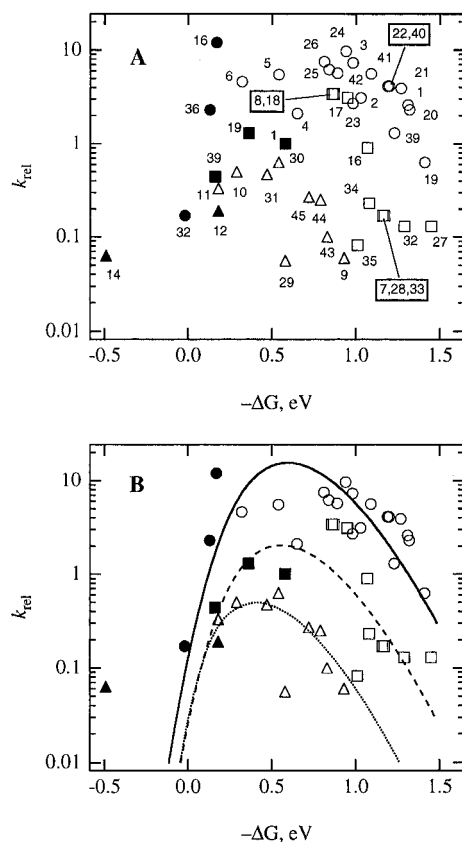


Figure 3. Plots of relative ET rates (k_{rel}) vs free energy change ($-\Delta G$) between benzyl radicals and radical cations of one-ring (open circle), two-ring (open square), and three-ring donors (open triangle) or radical anions of one-ring (filled circle), two-ring (filled square), and three-ring acceptors (filled triangle). The numbers in A denote the run number in Table 4. The straight, dashed, and dotted curves in B are calculated for one-, two-, and three-ring systems, respectively, by using the values in the text.

revealing the Marcus inverted region. Although actual examples for the inverted region have been demonstrated,^{7–19} the present result seems to be a very specific case as discussed below.

The absence of the inverted region in the intermolecular electron transfers between excited state molecules and quenchers, so-called the Rehm–Weller relationship,²⁰ is well-known. Among various explanations, the formation of electronically excited state products has gained the widest acceptance,²¹ and proved to be true for some cases.⁴⁷ Since radical ions generally have much lower excited states than the neutral molecules, the energy gap may become smaller by subtraction of the excitation energy, so that the process cannot be sufficiently exergonic to reach the inverted region. If the availability of the excited state accounts for the crucial difference, the electron transfer between two open-shell partners may show the inverted region so long as the products are non-radical species with much higher excitation energies.²¹ In fact, all the examples for the inverted region have been demonstrated for electron transfer between radical species affording closed-shell species.^{7–19}

Alternatively, Kakitani et al.^{26a} and Tachiya et al.^{26b} have recently explained the dependence of donor–acceptor distance on the solvent reorganization energy, which increases by increasing the distance as indicated by Marcus.⁴⁸ That is, for a wide range of ΔG , the electron transfer between freely diffusing substrates can take place at the diffusion-controlled

rate at the distance at which the reorganization energy matches the free energy gap. Such cases have been explored experimentally.^{49–51}

In fact, it is common for the electron transfer between radical species by diffusional collisions that the maximal rate is not observed even in extremely exothermic cases.^{52–54} However, in a particular case, the inverted region has been reported for the back ET of *N*-alkyl pyridinyl radicals with a radical cation of an iridium complex.⁵⁵ Thus, if correct, the present ET reaction seems to be the second example of Marcus-type intermolecular electron transfer. Specific for these two cases may be the type of ET, i.e., charge shift between neutral and charged molecules. However, it has been revealed theoretically⁵⁶ and experimentally^{11d,45,57,58} that the difference between charge separation, shift, and recombination (a dielectric saturation effect of solvents)²⁵ has only a minor effect on the ET rates.

It has been indicated that the rate constant for the heterogeneous electron transfer of radical **2** on electrode (ca. 0.1 cm s⁻¹ for both oxidation and reduction) is similar to the values for common hydrocarbon/ion radical couples.⁵⁹ The kinetics of ET between benzyl radicals and aromatic radical anions have shown that the electron transfer proceeds with smaller reorganization energy than the redox of alkyl radical/anion⁶⁰ because of a smaller change in the molecular structures by the redox process.⁶¹ For the cation/radical pair, the vibrational reorganization energy, λ_v , was estimated from molecular orbital calculations^{11d,62} (see Experimental Section) to be ca. 0.10 eV, which was still smaller than that calculated for radical/anion pair (0.13 eV). Thus, the vibrational reorganization energy is not the critical factor for the present case.

The other parameters governing the ET rates are the solvent reorganization energy (λ_s) and the electronic coupling matrix elements (V). The estimated λ_s values for benzyl radicals are 0.41, 0.37, and 0.24 eV for one-, two-, and three-ring systems, respectively (see Figure 3). The λ_s and relative V values are in the order of one- > two- > three-ring radical ions, which is interpretable on the basis of the relative charge densities of the three systems. That is, the charge density of one-ring aromatic radical ions is higher than that of two-ring ions and hence the ET rates are expected to be higher than two- or three-ring systems. The higher charge density results also in the higher solvent reorganization energy as observed. Thus, the relative

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λ_s and V values for these systems may be comprehensive on the basis of their different charge densities.

We could not answer, however, why the inverted region was observed so clearly for the intermolecular case of benzyl radicals. Theoretical studies usually treat donor/acceptor molecules or solvents as "spheres", which are far from the real pictures, and always neglected are the characteristics of reacting molecules such as the orientation of interacting orbitals or the polarizabilities of molecules. A change of spin states might be of some importance in the ET reaction of radicals as exemplified as the magnetic field effect⁶³ and spin statistical effect.⁶⁴ Some of these factors may be important in the ET reaction of benzyl radicals, resulting in the slowdown of ET rates and hence in the appearance of the inverted region. At present we cannot clarify the origin of the inverted region. To clarify these points, the direct determination of ET rates of benzyl radicals is desired but it is not so easy to determine the absolute rates because of the involvement of so many intermediates, e.g., $D^{\bullet+}$, $A^{\bullet-}$, R^{\bullet} , R^+ , and R^- . Electrochemical methods are also not directly accessible to very fast ET processes because of the instrumental limitation.

In the present paper, a fundamental assumption is that ion pairs of $D^{\bullet+}$ and $A^{\bullet-}$ are formed and exist in ca. 1:1 ratio during the irradiation. A case where this situation is not satisfied seems also to be assumed. That is, if a portion of $D^{\bullet+}$ is consumed by some side reaction,⁶⁵ an equal amount of $A^{\bullet-}$ is to be accumulated in the solution. In fact, when cation radicals are consumed, stable radical anions such as $DCA^{\bullet-}$ have been shown to be accumulated.^{66,67} In such cases, the ratios of $D^{\bullet+}$ and $A^{\bullet-}$ become different from the initial 1:1 ratio and the resulting product ratios ought to reflect the concentration ratios of $D^{\bullet+}/A^{\bullet-}$. However, control experiments seem to rule out this possibilities. That is, redox product ratios were not altered by changing light intensity and sensitizer concentrations. On the other hand, the product ratio changed significantly by substituents (see Table 4), reflecting the relative ET rates of substituted benzyl radicals.

Conclusion. Efficient redox reaction of benzyl-type radicals was achieved by the irradiation of aromatic donor/acceptor/ketone in MeOH–MeCN. In this system, one-electron oxidation and reduction of photogenerated benzyl radicals occurred by the reaction with radical ions of donor and acceptor to yield the corresponding benzyl cation and anion, which were trapped by MeOH affording ROME and RH, respectively. Relative product ratios of products which indicate the relative ET rates were determined for a variety of donor–acceptor pairs. The apparent relative ET ratios were determined from the product ratios and correlated with ΔG values of the redox reaction. The relative ET rates became maximal at the energy gap of ca. -0.5 eV, representing a novel example of the Marcus inverted region.

Experimental Section

General. ¹H NMR spectra were recorded with Hitachi R24B (60 MHz) and Varian GEMINI-200 (200 MHz) NMR spectrometers. GLC analyses were performed with Yanagimoto G180 and Shimadzu GC-

14A gas chromatographs, using a 2.5 mm \times 1 m column of Carbowax 300 M (2%) on Chromosorb WAW. A Shimadzu Chromatopac C-R3A integrator was used for quantitative analyses. GC-MS analyses were carried out with a JEOL D300 or a Shimadzu QP-5000 mass spectrometer using a 2.5 mm \times 1 m column of Carbowax 300 M (2%) on Chromosorb WAW or a 0.2 mm \times 25 m capillary column of Silicon OV-1 (J&W Scientific, DB-1). Absorption spectra were recorded on a Shimadzu UV-265 ultraviolet spectrometer.

Materials. Acetonitrile was distilled from phosphorus pentoxide. Methyl alcohol (Dotite Spectrozol), methyl alcohol-*d* (Aldrich, 99.5 atom % D), 2,6-dimethylnaphthalene (DMN; Aldrich), 4,4'-dimethyldiphenyl (DMD; Aldrich), and 1,2,4-trimethoxybenzene (124TrMOB; Aldrich) were employed as received. Naphthalene (N), 2-methoxynaphthalene (MON), diphenyl (D), phenanthrene (P), anthracene (A), 1-cyanonaphthalene (CN), and 9-cyanoanthracene (CA) were purified by recrystallization. Mesitylene (135TrMB), 1,2,4-trimethylbenzene (124TrMB), 1,2,3,5-tetramethylbenzene (1235TeMB), pentamethylbenzene (PMB), 1,2-dimethoxybenzene (12DMOB), 1,4-dimethoxybenzene (14DMOB), 1,3,5-trimethoxybenzene (135TrMOB), and 2-methylnaphthalene (MN) were received from Tokyo Kasei and distilled. *sym*-Tetraphenylacetone (**1**),⁶⁸ substituted dibenzyl ketones (**11**),⁶⁹ 9-methoxyanthracene (MOA),⁷⁰ 9,10-dimethoxyanthracene (DMOA),⁷⁰ 2,5-dimethyl-1,4-dicyanobenzene (DMDCB),⁷¹ dicyanodurene (TeMDCB),⁷¹ and 9,10-dicyanoanthracene (DCA)⁷² were prepared as reported.

Typical Procedure for Photolyses. Irradiations were done with a 300-W medium-pressure mercury lamp in a 25-mL Pyrex test tube, i.e., >290 nm. A 10-mL MeOH–MeCN (1:9) solution of 0.3 mM *sym*-tetraphenylacetone, 10 mM naphthalene, and 10 mM *p*-dicyanobenzene in a test tube with a septum rubber cap was purged with argon for 15 min and was irradiated at 20 ± 3 °C. The products were identified by GC-MS, and the conversion of the ketone and the yields of products were determined at appropriate intervals of time by GLC.

Electrochemical Measurements. The redox potentials of ketones (**1**, **11**) and acceptors (DMDCB and TeMDCB) were obtained in MeCN containing 0.1 M *n*-Bu₄NBF₄ by the rotating ring-disk electrode voltammetry⁷³ using a Nikko Keisoku RRDE-1 electrode and a DPGS-6 potentiostat at 1000 rpm. The redox potentials of other acceptors (DCB, CN, CA, and DCA)^{2a} and methyl-^{11d} or methoxy-substituted donors⁷⁴ were taken from literature. The potentials are summarized in Table 1 and Chart 1.

Calculations of Theoretical Electron Transfer Rates. Calculation of theoretical electron transfer rates according to eq 9 and the fitting to the experimental data were carried out on an Apple Macintosh computer using the program IGOR PRO (Wavemetrics). When the values for a vibrational reorganization energy (λ_v) of 0.25 eV and an averaged frequency (ν) of 1500 cm⁻¹ were adapted,^{9b,11d} a solvent reorganization energy (λ_s) and an electronic coupling matrix element (V) were the variables to be optimized. Iterated calculation of the Franck–Condon weighted density was carried out for $w = 0$ to 10, since further iterations over 11 did not affect the rates.

Estimation of λ_v by Molecular Orbital Calculations. The vibrational reorganization energy, λ_v , was estimated by molecular orbital calculations using a method similar to those described by Nelsen⁶² and Gould et al.^{11d} The semiempirical PM3 calculations³⁰ were carried out on Apple Macintosh and NEC PC-9801 computers using the MOPAC package (versions 5⁷⁵ and 6⁷⁶). Calculations on benzyl cation or anion

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and on radical were performed with the RHF and UHF methods, respectively. The geometries were optimized within a C_{2v} symmetry, i.e., in planar geometry, with the keyword PRECISE to increase the criteria for the terminating the optimization by a factor of 100. The UHF heats of formation of benzyl radical in equilibrium geometries of benzyl cation, radical, and anion were 40.62, 39.63, and 40.92 kcal/mol, respectively. The RHF heats of formation of benzyl cation in geometries optimized for benzyl cation and radical were 227.42 and 228.63 kcal/mol, and those of anion in radical and anion geometries were 20.15 and 18.53 kcal/mol, respectively. The vibrational reorganization energy, λ_v , can be estimated from the sum of the difference in energy before and after electron transfer, i.e., the difference in energy

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at radical and ion geometries. The resulting reorganization energies were $(40.62 - 39.63) + (228.63 - 227.42) = 2.20$ kcal/mol and $(40.92 - 39.63) + (20.15 - 18.53) = 2.91$ kcal/mol (ca. 0.10 and 0.13 eV) for benzyl cation/radical and radical/anion pairs, respectively.

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Supporting Information Available: Tables of the product yields on the co-irradiation of **1** and donor–acceptor systems (3 pages). See any current masthead page for ordering and Internet access instructions.

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