Figure 1. ORTEP view of **3**. Bond distances (Å) and angles (deg) of interest for the two independent molecules: Fe(1)–Fe(2), 2.6918 (9), 2.655 (1); Fe(3)–Fe(4), 2.629 (1), 2.619 (1); Fe(1)–P(1), 2.224 (1), 2.171 (1); Fe(1)–P(2), 2.243 (1), 2.252 (1); Fe(2)–P(1), 2.232 (1), 2.162 (2); Fe(2)–P(2), 2.199 (1), 2.205 (1); Fe(3)–P(3), 2.198 (1), 2.249 (2); Fe(3)–P(4), 2.245 (1), 2.224 (2); Fe(4)–P(3), 2.184 (2), 2.185 (1); Fe(4)–P(4), 2.206 (2), 2.184 (1); P(1)–P(3), 2.250 (2), 2.300 (2); P(1)–P(4), 2.245 (2), 2.247 (2); Fe(1)–P(1)–Fe(2), 74.34 (5), 75.57 (5); P(3)–P(1)–P(4), 69.37 (6), 67.57 (6); Fe(3)–P(3)–Fe(4), 73.73 (5), 72.38 (5); Fe(3)–P(4)–Fe(4), 72.40 (5), 72.90 (5); Fe(1)–P(2)–Fe(2), 74.59 (4), 73.13 (4).

relatively short P(3)–P(4) distance, 2.126 (2) Å, compares well with the values found in various diphosphene complexes η^2-bonded.[1a,4] Therefore the P(3)P(4) fragment can be described as the first $\mu_4\eta^2$ complexed $\sigma^2\lambda^3,\sigma^4\lambda^5$ diphosphorus unit (—P=P<) which promises to lead to new reactivity patterns.

The ^{31}P{^{1}H} NMR spectrum confirms the presence of four phosphorus atoms—each of them being coupled with the other three— and is assigned as follows: P(3) δ 117.3 (d, d, d $J_{P_3P_4}$ = 357, $J_{P_3P_2}$ = 5, $J_{P_3P_1}$ = 20 Hz), P(4) δ 169.5 (d, d, d $J_{P_4P_3}$ = 357, $J_{P_4P_2}$ = 5, $J_{P_4P_1}$ = 22 Hz), P(2) δ 264.7 (d, t $J_{P_2P_3}$ = 5, $J_{P_2P_4}$ = 5, $J_{P_2P_1}$ = 22 Hz), P(1) δ 515.7 (d, t $J_{P_1P_3}$ = 20, $J_{P_1P_4}$ = $J_{P_1P_2}$ = 22 Hz). The large $J_{P_3P_4}$ value suggests that atoms P(3) and P(4) are doubly bonded.

In summary thermal activation of **1** leads to a succession of unexpected and interesting transformations: the transformation of **3** implies without prejudging the order of reactions the cleavage of the phosphorus–phosphorus double bond of the diphosphene ligand with the insertion of the Fe$_2$(CO)$_6$ fragment, the migration of one phenyl group from one phosphorus to another phosphorus group, and the insertion of a "P" fragment into the two phosphorus of a second Fe$_2$(CO)$_6$(PPh)$_2$ entity. The precise mechanism of these rearrangements is difficult to establish, but several examples of migration of phenyl group from phosphorus to a metal center have been described in the literature, and it can be suggested that this migration is metal assisted.[12] To our knowledge this is the first case where migration occurs from a phosphorus atom to another phosphorus atom.

Finally the **3** → **4** transformation implies the departure of two CO ligands, the P(1)P(4) or P(1)P(3) bond breaking with simultaneous association of the two Fe$_2$ fragments and generation of a P=P—Ph fragment.

To conclude, this unprecedented thermal activation of a diphosphene complex is probably the consequence of a synergic effect
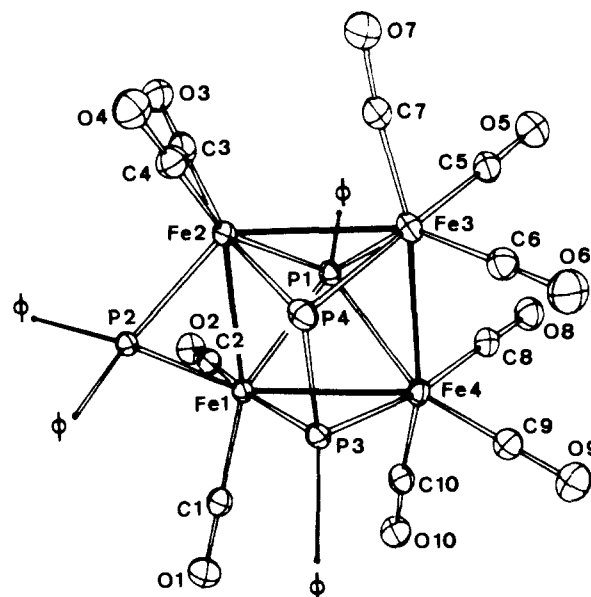
Figure 2. ORTEP view of **4**. Bond distances (Å) and angles (deg) of interest: Fe(1)–Fe(2), 2.7249 (2); Fe(2)–Fe(3), 2.726 (1); Fe(3)–Fe(4), 2.824 (1); Fe(4)–Fe(1), 2.7601 (9); Fe(1)–P(1), 2.266 (2); Fe(2)–P(1), 2.250 (2); Fe(3)–P(1), 2.241 (2); Fe(4)–P(1), 2.261 (2); Fe(1)–P(2), 2.196 (2); Fe(2)–P(2), 2.189 (2); Fe(1)–P(3), 2.205 (2); Fe(4)–P(3), 2.247 (2); Fe(2)–P(4), 2.297 (2); Fe(3)–P(4), 2.342 (2); P(3)–P(4), 2.126 (2); Fe(1)–Fe(2)–Fe(3), 91.12 (3); Fe(2)–Fe(3)–Fe(4), 89.58 (3); Fe(3)–Fe(4)–Fe(1), 88.53 (3); Fe(4)–Fe(1)–Fe(2), 90.95 (3); Fe(1)–P-(1)–Fe(3), 119.41 (7); Fe(2)–P(1)–Fe(4), 120.24 (7); Fe(1)–P(2)–Fe(2), 76.84 (5); Fe(1)–P(3)–Fe(4), 76.64 (6); Fe(2)–P(4)–Fe(3), 71.95 (6); C(29)–P(3)–P(4), 113.1 (1).

between the diphosphene ligand and Fe(CO)$_n$ units rearrangements.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and interatomic bond distances and angles for **3** and **4** (7 pages); tables of observed and calculated structure factors for **3** and **4** (25 pages). Ordering information is given on any current masthead page.

Effect of Molecular Dimension on the Rate of Return Electron Transfer within Photoproduced Geminate Radical Ion Pairs

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Corporate Research Laboratories
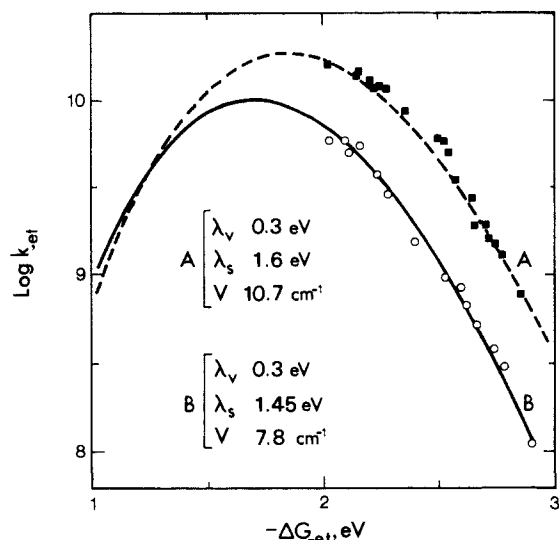*Eastman Kodak Company*
Rochester, New York 14650

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Photoinduced electron transfer to form radical ion pairs and separated radical ions is a common process,[1] and numerous chemical reactions of the so-formed radical ions have been identified.[1] The quantum yields of these reactions vary over a very wide range,[2] mainly because of differences in the rate con-

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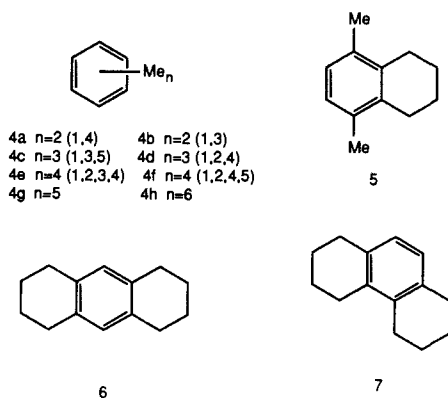
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Figure 1. Log k_{-et} versus $-\Delta G$ for return electron transfer within geminate radical ion pairs with (A) substituted benzenes (4-7) and (B) substituted naphthalenes (1), biphenyls (2), and fluorene (3) as donors. The curves are calculated by using the parameters shown in the figure with a value of $\bar{\nu}$ of 1500 cm^{-1} for both sets of data (see text).

Chart I

4a n=2 (1,4)   4b n=2 (1,3)
4c n=3 (1,3,5) 4d n=3 (1,2,4)
4e n=4 (1,2,3,4) 4f n=4 (1,2,4,5)
4g n=5   4h n=6

6   7

stants for the energy wasting return electron transfer (k_{-et}) within the initially formed geminate ion pairs $(A^{\cdot-}/D^{\cdot+})$ (eq 1).[2] We

$$A + D \xrightleftharpoons{k_{-et}} A^{\cdot-}/D^{\cdot+} \xrightarrow{k_{sep}} A^{\cdot-} + D^{\cdot+} \tag{1}$$

have shown that k_{-et} *decreases* as the energy content of the ion pair $(E^{ox}_D - E^{red}_A)$ *increases*[2a] and that this behavior represents a clear example of the Marcus "inverted region".[3] We now present data which demonstrate that in addition to this free-energy dependence, k_{-et} depends upon the molecular dimensions of the radical pair partners. Radical ion pairs of the radical anions of 9,10-dicyanoanthracene (DCA) or 2,6,9,10-tetracyanoanthracene (TCA), the radical cations of naphthalene (1a), 2-methyl-naphthalene (1b), 2,6-dimethylnaphthalene (1c), biphenyl (2a), 3,3'-dimethylbiphenyl (2b), 4,4'-dimethylbiphenyl (2c), and fluorene (3), and the substituted benzenes summarized in Chart I were studied. The experimental procedure was the same as that described in ref 2a, in which 4,4'-dimethoxystilbene (DMS) was used as a monitor to intercept the radical cations which escape the geminate pair.[4,5]

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(4) The values of k_{-et} were determined from quantum yields of separated radical ion formation (Φ_{sep}, ref 5) by assuming that Φ_{sep} is determined only by k_{-et} and the rate of separation (k_{sep}) of radical ions from the geminate pair to form separated radical ions. In this work k_{sep} is taken to be 5×10^8 s^{-1} for all of the radical ion pairs studied (ref 2a).

Scheme I

8

9
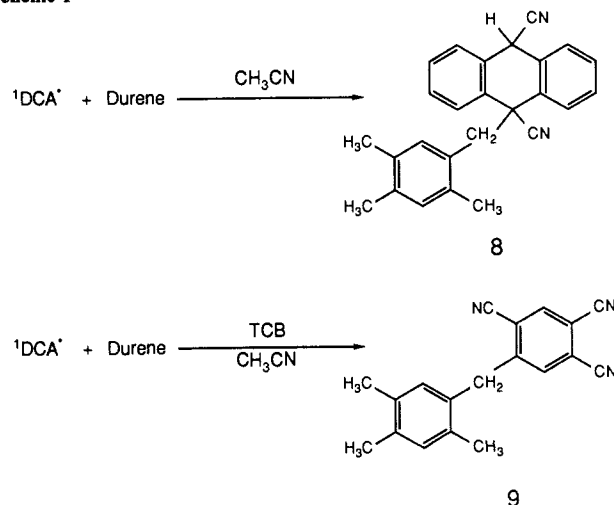
In Figure 1b are shown previously published data together with new data for additional donors which show the variation in k_{-et} as a function of reaction free energy[6] for radical ion pairs with 1-3 as cations. The quantum yields for separated radical ion formation increase, and the values of k_{-et} decrease with increasing reaction free energy $(-\Delta G)$. Clearly, both naphthalene and biphenyl derivatives fall on the same curve. The rate constants, k_{-et}, for the benzene derivatives 4-7 (Figure 1a) also decrease with increasing $-\Delta G$. However, for these "one-ring" compounds, Φ_{sep} are consistently lower, and thus k_{-et} higher, than corresponding values for the "two-ring" compounds (naphthalenes and biphenyls) of similar $-\Delta G$. The possibility of a chemical reaction of the geminate pair competing with the separation and return electron transfer (thus reducing Φ_{sep}) in the case of the alkyl-substituted benzenes was considered. The DCA/durene system was studied in detail as a representative example. Indeed, steady-state irradiation of a degassed acetonitrile solution of these reactants gave the 1:1 adduct 8[7] (Scheme I). However, this product formation would affect the determination of Φ_{sep} *only* if it results from reaction within the primary geminate pair or via the separated radical ions if it proceeds at a rate which can compete with the interception rate of ca. 5×10^6 s^{-1} by the DMS.[5] These two possibilities were ruled out by the following product quenching experiments. Irradiation in the presence of a low concentration ($\sim 10^{-3}$ M) of 1,2,4,5-tetracyanobenzene (TCB), which is easier to reduce than DCA, resulted in complete replacement of 8 by 9[7] (Scheme I). Interception of the geminate pair of DCA$^{\cdot-}$/durene$^{\cdot+}$ by TCB is negligible at the concentration used. The formation of 8 was also strongly quenched ($\sim 97\%$) by DMS at a concentration of 5×10^{-4} M which only scavenged separated radical ions. Increasing the concentration of DMS to 10^{-3} M gave the same results indicating that only a very minor "chemical"

(5) Experiments were performed in degassed acetonitrile at room temperature. DCA or TCA were excited in the presence of 0.02-0.5 M one- or two-ring donor by using a pulsed dye laser (Lumonics EPD-330, 410 nm, ca. 12 ns, ca. 1 mJ). Separated radical cations of the donors were scavenged by using 5×10^{-4} M DMS. The DMS radical cation was monitored at 530 nm by using conventional transient absorption techniques. The different yields of DMS radical cation observed for the different ion pairs were converted to quantum yields for free-ion formation (Φ_{sep}) as previously described (ref 2a). Where necessary the measured ion yields were corrected for incomplete interception of the excited sensitizer and extrapolated to zero donor concentration.

(6) (a) The reaction free energies $(-\Delta G)$ are given by $E^{ox}_D - E^{red}_A$. The redox parameters are summarized in ref 2a. The previously unreported oxidation potentials are 2b, 1.405 V; 2c, 1.223 V; 3, 1.283 V; 4a, 1.62 V; 4b, 1.70 V; 4c, 1.67 V; 4d, 1.48 V; 4e, 1.403 V; 4f, 1.34 V; 4g, 1.27 V; 4h, 1.148 V; 5, 1.37 V; 6, 1.282 V; and 7, 1.332 V versus ferrocene under the conditions described in ref 2a. The oxidation potentials for 4a-c were obtained by normalizing those values from ref 6b to the present conditions by subtracting 0.68 V. (b) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(7) NMR data for both isomers of compound 8, compound 9, and two derivatives of 8 are provided as Supplementary Material.

process takes place within the primary geminate pair. The rate constant of the chemical reaction within the geminate pair is thus estimated to be < 1% of k_{-et}.

An important aspect of the size effect is clearly demonstrated by the donors 5–7 which have similar molecular dimensions to dimethylnaphthalene, anthracene, and phenanthrene, respectively, but whose k_{-et} fit with the other substituted benzene derivatives. Evidently it is the size of the aromatic nucleus and not the overall size of the molecule which is important.

As described previously[2a] the data can be fitted to a theoretical relationship between k_{-et} and $-\Delta G$.[8] The fitting parameters are V, an electron coupling matrix element, λ_s and λ_v, the Marcus solvation and vibrational reorganization energies, and a single frequency, ν, which is taken to be representative of the frequencies of the rearranged vibrational modes.[8] In order to allow a meaningful comparison between the data, restrictions must be placed on the number of parameters which can be varied. Vibrational reorganization energies are expected to be small for organic molecules[9] and similar for both sets of data.[10] Good fits were obtained for both curves by using a value for λ_v of 0.3 eV. For consistency with previous work,[2a,8a,b] $\bar{\nu}$ was fixed at 1500 cm^{-1}. By using these values for λ_v and $\bar{\nu}$, larger values for V and λ_s are required to fit the data of the one-ring donors compared to those of the two-ring donors. Although the absolute values obtained for the matrix coupling elements and reorganization energies depend upon the form of the theoretical equation, the choice of the value of ν, and also the fitting procedure, the data in Figure 1 indicate that both the electronic coupling and the total reorganization energy are larger for the one-ring donors compared to those of the two-ring donors.

Qualitatively the smaller V for the two-ring donors suggests a smaller orbital overlap integral compared to the one-ring donors[11a,b] and is consistent with the prediction that more complex nodal structures for the molecular orbitals of larger aromatic systems result in smaller matrix elements.[11c]

The larger λ_s for the one-ring compounds suggests a higher degree of solvation for these geminate pairs compared to those of the two-ring compounds. Support for this suggestion was obtained from exciplex emission data. Although exciplexes are solvated less strongly than geminate pairs, these species can be considered to be the contact ion pair equivalents of the solvent-penetrated geminate pairs.[12] Accordingly, exciplex solvation, obtained from differences in the emission maxima in solvents of different polarities, can be used as a guide to the solvation of the geminate pair. A constant energy difference of 0.345 ± 0.013 eV is found in the emission of exciplexes of DCA with the two-ring compounds 1–3 in acetonitrile and cyclohexane. For the corresponding exciplexes of the one-ring donors in these two solvents, a constant and higher value of 0.49 ± 0.02 eV is found, which is consistent with higher solvation in these cases.

The return electron transfer rates, k_{-et}, in these systems are evidently very sensitive to small structural changes. Differences in the matrix coupling elements and the degree of solvation between the ion pairs appear to result from differences in charge

distribution and the degree of delocalization.

Generation of Simple Enols by Photooxidation. Keto–Enol Equilibrium Constants of Some Aliphatic Systems in Aqueous Solution

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There has been a revival of interest in the chemistry of simple enols recently, sparked by the development of techniques for generating them in greater than equilibrium amounts under conditions where rates of their reactions may be measured accurately.[1–4] We wish to report that we have produced yet another method of doing this and have used it to provide keto–enol equilibrium constants for a series of simple ketones in aqueous solution. These are the first reliable, wholly experimentally determined values of this quantity for these substances.

Our method involves the photooxidation of alcohols by carbonyl compounds to produce ketyl radicals, eq 1. This is a well-known
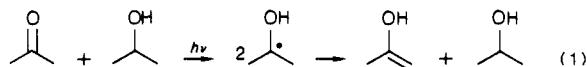
process,[5] and there is CINDP evidence that the ketyl radicals so formed may undergo disproportionation to give enols.[6] We have found that flash photolysis of solutions of acetone (0.05 M) in dilute aqueous perchloric acid containing 0.01–0.10 M isopropyl alcohol produces a short-lived transient species with strong absorbance at λ = 215 nm whose intensity depends upon the amount of isopropyl alcohol supplied. Decay of this transient adheres to the first-order rate law closely, and observed first-order rate constants measured over the range [HClO$_4$] = 0.004–0.1 M are accurately proportional to acid concentration; least-squares analysis of the data gives k_{H^+} = (5.47 ± 0.06) × 10^3 M^{-1} s^{-1}, which agrees well with k_{H^+} = (5.38 ± 0.08) × 10^3 M^{-1} s^{-1} measured before[3d] for the ketonization of acetone enol, eq 2. This evidence identifies the transient species as the enol of acetone.
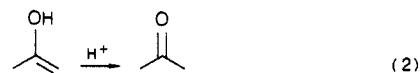
Use of other alcohols in place of isopropyl alcohol gives corresponding behavor. In such cases, however, two different ketyl

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(10) (a) Parameters can be found to fit the two-ring data which include values for λ_v as high as 0.6 eV (ref 2a). However, λ_v must be less than 0.4 eV in order to fit the one-ring data. Furthermore, molecular orbital calculations similar to those described in ref 9b suggest that λ_v is ca 0.3 eV for both (Gould, I. R.; Farid, S., unpublished results). The use of a smaller λ_v requires that V be smaller and λ_s larger than the corresponding values used to fit the data reported in ref 2a. (b) Nelson, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677.

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