relatively short P(3)-P(4) distance, 2.126 (2) Å, compares well with the values found in various diphosphene complexes π-bonded. Therefore the P(3)P(4) fragment can be described as the first μνπd complexed σπσd diphasphorus unit (—P=P—) which promises to lead to new reactivity patterns.

The 31P{1H) 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 Jp,p = 357, Jp,p = 5, Jpp = 20 Hz), P(4) δ 169.5 (d, d, d Jp,p = 357, Jp,p = 5, Jpp = 22 Hz), P(2) δ 264.7 (d, Jp,p = 5, Jpp = 20 Hz). The large Jp,p 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(CO)6 fragment, the migration of one phenyl group from one phosphorus to another phosphorus of a second Fe2(CO)6(PPh)2 entity. The precise mechanism of these rearrangements is difficult to establish, but several examples of the phosphorus-phosphorus double bond of the diphosphene simultaneously associated with the insertion of the Fe2(CO)6 fragment, the migration of one phenyl group from one phosphorus to another phosphorus (2).

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

Ian R. Gould,* Jacques E. Moser,¹ Deniz Ege, and Samir Farid*

Corporate Research Laboratories Eastman Kodak Company Rochester, New York 14650 Received October 19, 1987

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

1Current address: Institut de Chimie Physique, École Polytechnique Fédérale Lausanne, Lausanne, Switzerland.

Figure 1. ORTEP view of 3. Bond distances (Å) and angles (deg) of interest for the two Fe2(CO)6 units: Fe(1)-P(1), 2.224 (1), 2.217 (1); Fe(2)-P(2), 2.243 (1), 2.252 (1); Fe(2)-P(3), 2.232 (1), 2.162 (2); Fe(2)-P(4), 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); Fe(1)-P(2)-Fe(2), 76.64 (6), 76.57 (6); Fe(2)-P(2)-Fe(2), 74.59 (6), 76.64 (6); Fe(3)-P(3)-Fe(4), 72.40 (5), 72.38 (5); Fe(3)-P(4)-Fe(4), 72.40 (5), 72.38 (5); Fe(4)-P(4)-Fe(4), 72.40 (5), 72.38 (5); Fe(1)-P(2)-Fe(2), 74.59 (4), 73.13 (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(2)-P(4), 2.241 (2); Fe(4)-P(1), 2.265 (2); Fe(1)-P(2), 2.196 (2); Fe(2)-P(2), 2.189 (2); Fe(4)-P(3), 2.205 (2); Fe(4)-P(4), 2.247 (2); Fe(2)-P(3), 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), 131.1 (1).

between the diphosphate ligand and Fe(CO)6 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.
Figure 1. Log $k_{sl}$ versus $-\Delta G$ for return electron transfer within geminate radical ion pairs with (A) substituted benzenes (4-7) and (B) substituted naphthalenes and biphenyls (2c) and fluorene (3) as donors. The curves are calculated by using the parameters shown in the figure with a value of $k_0$ of 1500 cm$^{-1}$ for both sets of data (see text).

Chart I

![Chart I](image)

Scheme 1

![Scheme 1](image)

In Figure 1b are shown previously published data together with new data for additional donors which show the variation in $k_{sl}$ as a function of reaction free energy for radical ion pairs with 1-3 as cations. The quantum yields for separated radical ion formation increase, and the values of $k_{sl}$ decrease with increasing reaction free energy ($-\Delta G$). Clearly, both naphthalene and biphenyl derivatives fall on the same curve. The rate constants, $k_{sl}$, for the benzene derivatives 4-7 (Figure 1a) also decrease with increasing $-\Delta G$. However, for these “one-ring” compounds, $\Phi_{sep}$ are consistently lower, and thus $k_{sl}$ 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 $\Phi_{sep}$) 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 (Scheme 1). However, this product formation would affect the concentration of $\Phi_{sep}$ 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. $5 \times 10^8$ s$^{-1}$ by the DMS. These two possibilities were ruled out by the following product quenching experiments. Irradiation in the presence of a low concentration ($\sim 10^{-4}$ M) of 1,2,4,5-tetracyanobenzene (TCB), which is easier to reduce than DCA, resulted in complete replacement of 8 by 9 (Scheme 1). Interception of the geminate pair of DCA/durene$^+$ by TCB is negligible at the concentration used. The formation of 8 was also strongly quenched ($\sim 97\%$) by DMS at a concentration of $5 \times 10^{-4}$ 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 $5 \times 10^{-4}$ 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 ($\Phi_{sep}$) as described previously (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 $E^0_0 - E^0_a$. The redox parameters are summarized in ref 2a. The previously unreported oxidation potentials are 2b, 1.05 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, 1.48 V; 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-e 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.; Klausing, L.; Wightman, R. M.; Kochi, J. K.; J. Am. Chem. Soc. 1984, 106, 3968.

(7) NMR data for both isomers of compound 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 \( k_{e-\text{o}} \).

An important aspect of the size effect is clearly demonstrated by the donors 5–7 which have similar molecular dimensions to dimethylanthracene, anthracene, and phenanthrene, respectively, but whose \( k_{e-\text{o}} \) 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\(^{(7)}\) the data can be fitted to a theoretical relationship between \( k_{e-\text{o}} \) and \( \Delta g \). The fitting parameters are \( \lambda \), an electronic coupling matrix element, \( \lambda_e \), the Marcus reorganization and vibrational reorganization energies, and a single frequency, \( \nu \), 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 \( \lambda_e \) of 0.3 eV. For consistency with previous work,\(^{(11)}\) \( \Delta g \) was fixed at 1500 cm\(^{-1}\).

By using these values for \( \lambda \) and \( \nu \), larger values for \( \nu \) and \( \lambda_e \) 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 \( \nu \) used 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 \( \nu \) for the two-ring donors suggests a smaller orbital overlap integral compared to the one-ring donors\(^{(12)}\) and is consistent with the prediction that more complex nodal structures for the molecular orbitals of larger aromatic systems result in smaller matrix elements.

The larger \( \lambda_e \) 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.\(^{(3)}\) Accordingly, exciplex solvation, obtained from 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 \( 0.345 \pm 0.013 \) 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 \( 0.49 \pm 0.02 \) eV is found, which is consistent with higher solvation in these cases.

The return electron transfer rates, \( k_{e-\text{o}} \), 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.

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Supplementary Material Available: NMR data and structures for adducts 8 and 9 and derivatives of 8 (2 pages). Ordering information is given on any current masthead page.

Generation of Simple Enols by Photooxidation.

Keto-Enol Equilibrium Constants of Some Aliphatic Systems in Aqueous Solution

J. R. Keeffe, A. J. Krege, and N. P. Schepp

Department of Chemistry, University of Toronto
Toronto, Ontario MSS 1A1, Canada
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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 CINDEP 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 \( \lambda = 215 \) 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 \( k_{o-p} = (5.47 \pm 0.06) \times 10^4 \) M\(^{-1}\) s\(^{-1}\), which agrees well with \( k_{o-p} = (5.38 \pm 0.05) \times 10^4 \) M\(^{-1}\) s\(^{-1}\) measured before\(^{(7)}\) 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 behavior. In such cases, however, two different ketyl

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