where k_{ox} is the rate constant for the carbene scavenging by oxygen ($k_{ox} = 5 \times 10^9$ M^{-1} s^{-1}), and k_0 is the reciprocal of the carbene lifetime in the solvent used, in the absence of oxygen and of I. Since only the last term in equation 2 is a function of the concentration of I, a plot of k_{growth} vs [I] yields, from the slope, the value of k_1. Such a plot is shown in Figure 1 and leads to $k_1 = (6.7 \pm 0.8) \times 10^6$ M^{-1} s^{-1}. This suggests that reaction 1 is much faster than typical carbene additions to olefins, reflecting the fact that addition of the carbene to one of the bridgehead positions allows the other to acquire a more favored pyramidal conformation.

We anticipated that biradical II would be initially formed in its triplet state and would, possibly, have a sufficiently long lifetime to be detected by transient absorption techniques. In fact, 308-nm excitation of dilute solutions of diphenyldiazomethane plus 2 M propellane in Freon-113 at −2 °C lead to the rapid formation of a strongly absorbing transient with λ_{max} at 330 nm (similar to diphenylmethyl radicals) and with a lifetime of 9.7 μs (see insert in Figure 1). Under these conditions the carbene lifetime (monitored at 320 nm) was 105 ns. These samples only allow for a few laser excitation shots, because of the rapid depletion of the dilute ($\sim 5 \times 10^{-5}$ M) diazo solution; fortunately, the signals are so intense that a few attenuated shots are sufficient to yield virtually noise free traces (see insert in Figure 1). Biradical II and triplet III are both possible candidates for the observed transient. However, the observation of a 124-ns lifetime for triplet III (generated by acetone sensitization in Freon-113 at room temperature) allowed us to rule out the latter possibility. Thus, we suggest that the long-lived transient is, in fact, biradical II. The unusually long lifetime for II may result from the fact that the two unpaired electrons are in orthogonal orbitals. This would be expected to substantially reduce the intersystem crossing which is generally the rate-determining step for triplet biradical decay.[17] Further experiments aimed at demonstrating whether or not intersystem crossing does affect the lifetime of II will be reported in a full paper.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance. The support received from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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[17] Johnston, L. J.; Scaiano, J. C. *Chem. Rev.*, in press.

A Connection between Intramolecular Long-Range Electron, Hole, and Triplet Energy Transfers

Gerhard L. Closs,*,†,‡ Mark D. Johnson,‡ John R. Miller,‡
and Piotr Piotrowiak†

Department of Chemistry
The University of Chicago
Chicago, Illinois 60637
Chemistry Division
Argonne National Laboratory
Argonne, Illinois 60439

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Over the past few years there has been an active program in our laboratories on long-range intramolecular electron transfer and its dependence on energetics, solvent, distance, and stereochemistry.[1] More recently we have extended this study to include positive ions, or hole transfer,[2] and triplet energy transfer.[3] The compounds in the three studies were the same or closely related, and the processes can be summarized and designated as in (1).

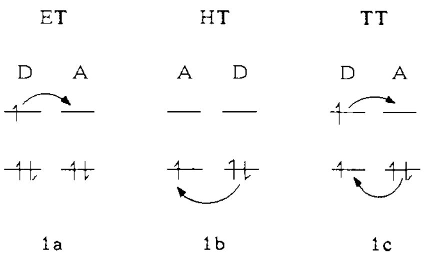

Figure 1. Frontier orbital representation of electron exchange in (1a) electron transfer, (1b) hole transfer, and (1c) triplet energy transfer by the Dexter mechanism.

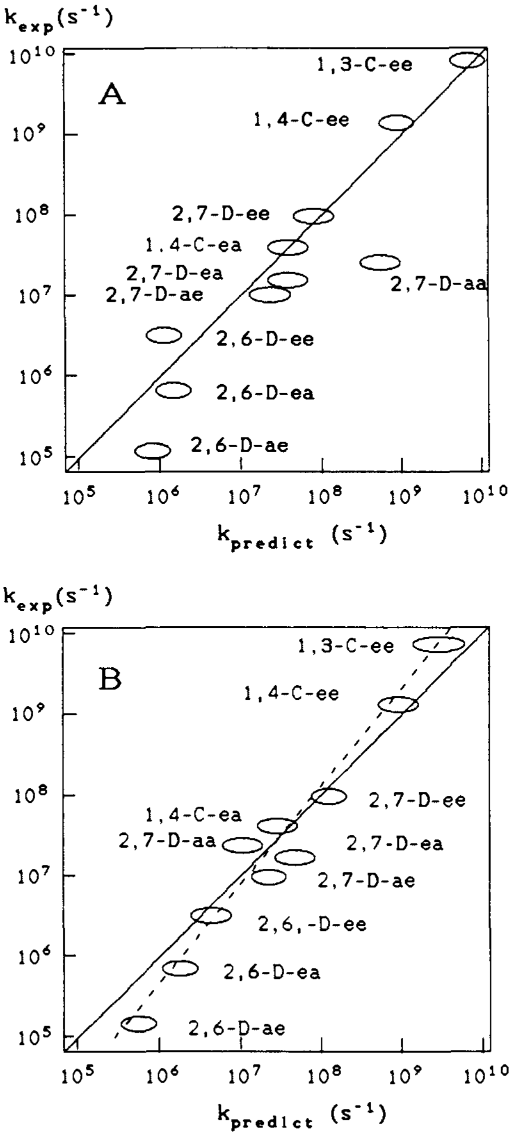

Figure 2. A. Experimental triplet transfer rate constants plotted against predicted rate constants using eq 4. B. Experimental versus predicted triplet transfer rate constants including corrections for reorganization energy changes with distance in ET and HT. Solid line: perfect fit to eq 4; dotted line: least-squares fit of points. Ellipses represent the estimated uncertainties. Note that the estimated rate constants contain the cumulative errors of two measurements.

$$\begin{array}{lll} \mathrm{D^{-}\text{-}Sp\text{-}A} \rightarrow \mathrm{D\text{-}Sp\text{-}A^{-}} & (\mathrm{ET}) & \\ \mathrm{D^{+}\text{-}Sp\text{-}A} \rightarrow \mathrm{D\text{-}Sp\text{-}A^{+}} & (\mathrm{HT}) & (1) \\ \mathrm{D'^{3}\text{-}Sp\text{-}A} \rightarrow \mathrm{D\text{-}Sp\text{-}A^{3}} & (\mathrm{TT}) & \end{array}$$

In the three series A = 2-naphthyl, and D = 4-biphenylyl in the ET and HT series and 4-benzophenoyl in the TT series. The

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[†] The University of Chicago.

[‡] Argonne National Laboratory.

[1] (a) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (c) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (d) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

[2] Johnson, M. D.; Miller, J. R.; Green, N. D.; Closs, G. L. *J. Phys. Chem.* **1989**, *93*, 1173.

[3] Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652.

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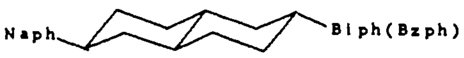
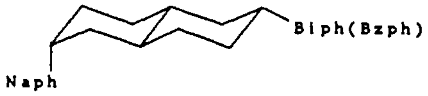
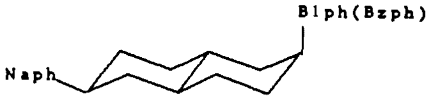
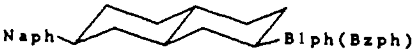
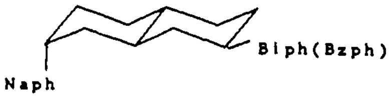
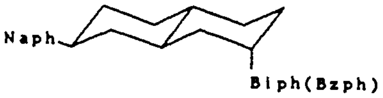
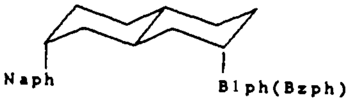
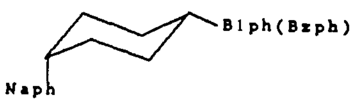
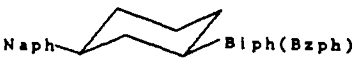
Table I

symbol	compound	$k_{ET}{}^{a}$	$k_{HT}{}^{b}$	$k_{TT}{}^{c}$	$k_{TT}{}^{pred\,d}$	$k_{TT\,corr}^{pred\,e}$
2,6-D-ee		5.0 E7	5.8 E7	3.1 E6	1.3 E6	3.9 E6
2,6-D-ea		5.9 E7	6.6 E7	0.70 E6	1.6 E6	2.0 E6
2,6-D-ae		2.8 E7	8.4 E7	1.3 E5	7.8 E5	7.5 E5
2,7-D-ee		2.9 E8	6.1 E8	9.1 E7	7.1 E7	14 E7
2,7-D-ea		3.0 E8	3.3 E8	1.5 E7	3.9 E7	5.0 E7
2,7-D-ae		1.8 E8	3.6 E8	1.1 E7	2.6 E7	2.6 E7
2,7-D-aa		25 E8	5.1 E8	2.6 E7	51 E7	1.0 E7
1,4-C-ee		1.6 E9	1.0 E9	1.3 E9	0.65 E9	1.0 E9
1,4-C-ea		2.5 E8	3.7 E8	4.0 E7	3.7 E7	2.8 E7
1,3-C-ee		4.2 E9	3.5 E9	7.7 E9	6.0 E9	3.8 E9

[a] Data are from ref 1c. [b] Part of the data are from ref 2. [c] Part of the data are from ref 3. [d] Computed with $C = 4.0 \times 10^{-10}$ s. [e] Computed with $C = 1.33 \times 10^{-9}$ s.

spacers (Sp) are *trans*-decalin and cyclohexane with different regio- and stereochemical (a = axial; e = equatorial) attachments. The specific compounds and the transfer rates are listed in Table I.

The three series have in common that the donor and acceptor groups are weakly coupled, making the reactions nonadiabatic with the rates following the Golden Rule.[1] We have previously shown for all series that the stereochemical attachment of donor and acceptor is important and that an exponential dependence on the number of σ-bonds, (N), separating donor and acceptor is only obtained within a series of the same stereochemistry.[4] With that we can write a general expression for the rates of any of the series as

$$k(\mathrm{St},N) = (2\pi/\hbar)\mathrm{St}|V_0|^2 \exp - \beta(N-1)\mathrm{FCWD} \qquad (2)$$

where St, the steric factor, expresses the influence of the steric attachment of donor and acceptor to the spacer, V_0 is the electronic coupling matrix element for separation by one σ-bond, and FCWD are the Franck–Condon weighted densities of states. For a series in which the Franck–Condon factors are held constant, eq 2 can be rewritten as (3).

$$k(\mathrm{St},N) = \mathrm{St}k_0 \exp - \beta(N-1), \quad \text{with} \quad k_0 = (2\pi/\hbar)|V_0|^2\mathrm{FCWD} \qquad (3)$$

As has been noticed previously,[5] the three processes can be symbolized as shown in Figure 1. In this picture ET is the electron transfer between the LUMOs of donor and acceptor, HT is the electron transfer between the HOMOs, and the TT by the Dexter mechanism[6] is a double electron transfer involving LUMOs and HOMOs. If this admittedly, oversimplified view were correct, the probability of TT should be proportional to the product of the probabilities of HT and ET. In terms of eq 3, this yields

$$k_{TT}(\mathrm{St},N) = Ck_{ET}(\mathrm{St},N)k_{HT}(\mathrm{St},N) \qquad (4)$$

where C is a constant containing the ratios of the V_0's and the FCWD. Equation 4 assumes that $\beta^{ET} + \beta^{HT} = \beta^{TT}$ and $\mathrm{St}^{TT}/(\mathrm{St}^{ET}\mathrm{St}^{HT}) = 1$ or is at least constant and that the Franck–Condon factors remain constant within each series. While the last assumption is not correct, Figure 2A, in which the experimental triplet energy transfer rate constants are plotted against the ones predicted by eq 4, shows a satisfactory correlation with one exception.[7]

It is well known that even with the same donors and acceptors, the FCWDs vary because the solvent reorganization energy in ET and HT reactions is a function of distance.[8] In TT reactions they are expected to vary much less because the nonpolar nature of the triplet state.[9] The noted deviation of the 2,7-D-a,a is expected because the D – A distance is particularly short in that compound. For eq 4 to hold, it is therefore necessary to correct for the distance dependence of the solvent reorganization energy in ET and HT. Unfortunately, the common procedure, based on a dielectric continuum model,[7] does not reliably estimate the

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[4] The stereochemical dependence is also predicted by ab initio MO calculations: Ohta, K.; Closs, G. L.; Morokuma, K.; Green, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 1319.

[5] Turro, N. J. *Modern Molecular Photochemistry*, Benjamin: 1978; p 306; Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Cotsaris, E.; Hush, N. *Chem. Phys. Lett.* **1988**, *143*, 488; **1988**, *150*, 179.

[6] Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

[7] The constant C has been adjusted to give the best fit through the points, excluding the rate for D-2,7-aa.

[8] Marcus, R. A. *Can. J. Chem.* **1959**, *37*, 155; *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

[9] The unimportance of the solvent reorganization energy in triplet energy transfer is demonstrated by the minimal rate change in varying the solvent from very polar to nonpolar.

distance dependence in these systems.[2] Figure 2B shows the best plot obtainable from a correction which is based on the continuum model but uses a smaller than computed solvent parameter.[10]

While there are problems remaining with the correction for the reorganization energy, there can be little doubt that the fundamental relationship expressed by eq 4 is a valid one for the case of weak coupling. These results may be regarded as a confirmation of the Dexter mechanism viewing triplet energy transfer as a simultaneous double-electron exchange. In addition, it shows that triplet energy transfer rates may be used to obtain information on electronic coupling in ET and HT. This is valuable because of the low solvent reorganization energy in TT it is much easier to separate contributions from electronic coupling terms from those originating in the Franck–Condon factors.

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[10] The dielectric continuum model[8] characterizes the solvent properties by the difference between the inverse of the high frequency and static dielectric constants of the solvent. Using these values for the solvents used in ET and HT overestimates the reorganization energies and using reasonable donor and acceptor radii gives a value too large by a factor of 2 in the case where the reorganization energy has been determined in an independent way.[1] Therefore we reduced this solvent parameter to a value giving the best correlation with eq 4. Experiments are in progress to derive a more satisfying procedure by determining the distance dependence of the reorganization energy by experiment.

Gas-Phase Photoinduced Reactivity of $RhC_5H_6^+$ with Cyclopentane

James R. Gord,† Steven W. Buckner,‡ and Ben S. Freiser*

Herbert C. Brown Laboratory of Chemistry
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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In the mature area of solution-phase photochemistry, a limitless number of examples exist in which a species, activated by the absorption of a photon, undergoes a reaction not observed in its ground state. In contrast, under the conditions used to study gas-phase ion-molecule chemistry at low pressures (10^{-5}–10^{-9} Torr), examples of photoinduced or photoenhanced reactions have been surprisingly sparse. In this environment, the time between reactive collisions is sufficiently long that internal conversion, photodissociation, or radiative and collisional relaxation of photoexcited ions significantly reduce the possibility of photoinduced reactivity.

Only one example of a photoenhanced ion-molecule reaction in this pressure regime has been reported to date.[1] Bomse and Beauchamp observed selective enhancement of k_r by $>10^3$ during an ion cyclotron resonance (ICR) study of the effect of infrared irradiation (10.6 μm) on reaction 1. In this communication, we

$$(CH_3OH)H^+(OH_2) + CH_3OH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CH_3OH)_2H^+ + H_2O \qquad (1)$$

report a second example of photoinduced reactivity in the ICR pressure regime and the first such example involving an organometallic ion.

All experiments were performed on a Nicolet-FTMS 2000 equipped with dual 4.76-cm cubic cells immersed in a 3 T magnetic field. Rh^+ was generated by direct laser desorption/ionization[2] from a rhodium foil (Alfa) situated in an external ion source.[3] Reagents were introduced through Varian leak valves or General Valve Series 9 pulsed valves.[4] Double resonance techniques[5] were used to isolate ions of interest and confirm parent–photoproduct relationships. Argon was maintained at $\sim 10^{-6}$ Torr to provide collisional thermalization of laser desorbed ions[6] and reaction products. Photochemical studies were performed using the 514.5-nm output of a Spectra-Physics Model 2030 Ar^+ laser operated at 1–3 W.

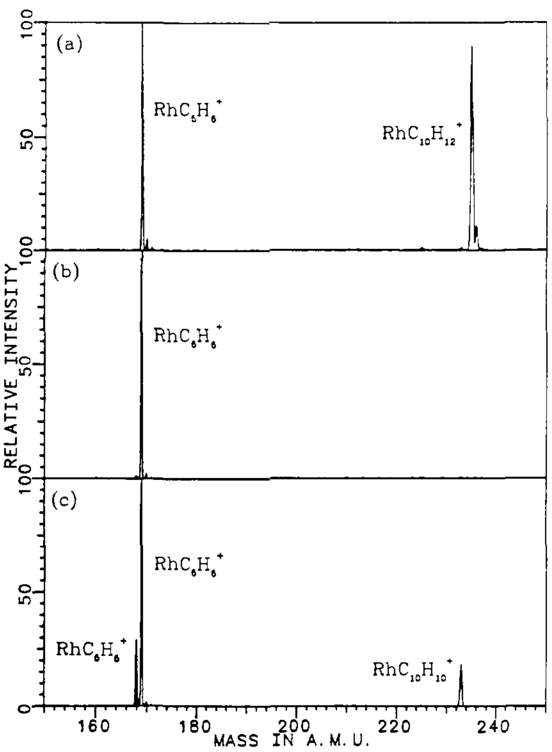

Figure 1. (a) Reaction of $RhC_5H_6^+$ and cyclopentane ($\sim 10^{-7}$ Torr) for 0.75 s with no irradiation, (b) with no irradiation and continuous ejection of $RhC_{10}H_{12}^+$, and (c) with 3-W 514.5-nm irradiation and continuous ejection of $RhC_{10}H_{12}^+$.

$RhC_5H_6^+$ was prepared through reaction of laser-desorbed Rh^+ with cyclopentane.[7] Thermalized $RhC_5H_6^+$ reacts with cyclopentane to produce $RhC_{10}H_{12}^+$, reaction 2. However, photoexcited $RhC_5H_6^+$ reacts with cyclopentane to produce the rhodocenium ion, reaction 3. In addition, irradiation results in photodissociation, reaction 4.[8] The fact that reaction 3 competes favorably with reaction 4 implies that the photodissociation pathway proceeds slowly, either because the photon energy is near the dissociation energy or because multiple photon absorption is

$$RhC_5H_6^+ + c\text{-}C_5H_{10} \rightarrow RhC_{10}H_{12}^+ + 2H_2 \qquad (2)$$

$$RhC_5H_6^+ \xrightarrow{h\nu} [RhC_5H_6^+]^* \xrightarrow{c\text{-}C_5H_{10}} RhC_{10}H_{10}^+ + 3H_2 \qquad (3)$$

$$RhC_5H_6^+ \xrightarrow[-H^\bullet]{h\nu} RhC_5H_5^+ \xrightarrow{h\nu} \text{other photoproducts} \qquad (4)$$

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† National Science Foundation Predoctoral Fellow.

‡ Current address: Department of Chemistry, University of Arizona, Tucson, AZ 85721.

(1) Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 3967.

(2) Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 37.

(3) Weller, R. R.; Ghaderi, S.; Vorburger, O.; Freiser, B. S. *Proceedings of the 36th ASMS Conference*; San Francisco, CA, June 1988.

(4) Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

(5) Comisarow, M. B.; Parisod, G.; Grassi, V. *Chem. Phys. Lett.* **1978**, *57*, 413.

(6) Kang, H.; Beauchamp, J. L. *J. Phys. Chem.* **1985**, *89*, 3364.

(7) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944.

(8) To confirm that $RhC_5H_5^+$ is produced directly via reaction 4 as opposed to via reaction 3 in competition with $RhC_{10}H_{10}^+$ production, $RhC_5H_6^+$ was also studied using pulsed valve introduction of cyclopentane to ensure that no cyclopentane was present during subsequent isolation and photodissociation.

0002-7863/89/1511-3753$01.50/0