Table I. Spectral Data and Yields of Azatitanacyclobutenes and Diazatitanacyclohexadienes[a]

RCN	azatitanacyclobutenes[b]				diazatitanacyclohexadienes[c]			
R =	Cp	CH_2	R	yield	Cp	CH	R	yield
Me	*d*	*d*	*d*	*d*	5.71	4.49	1.64, 1.73	93%
t-Bu	5.67	3.01	1.05	48%[f]	5.70	4.86	1.02, 1.21	*e*
C_6H_5	5.73	3.79	7.2–7.4 (m), 7.6–7.8 (m)	51%[g]	5.70	5.60	7.10–7.45 (m), 7.65–7.85 (m)	90%
p-Me-C_6H_4	*d*	*d*	*d*	*d*	5.75	5.67	2.14, 2.17; 7.86, 7.12 (AB); 7.45, 6.95 (AB)	93%
p-MeO-C_6H_4	*d*	*d*	*d*	*d*	5.78	5.70	3.30, 3.34; 7.84, 6.88 (AB); 7.41, 6.85 (AB)	93%
p-CF_3-C_6H_4	5.68	3.52	7.53	49%[g]	5.69	5.34	7.66, 7.48 (AB); 7.44, 7.16 (AB)	97%
C_6F_5	5.77	3.31		51%[g]	5.74	4.80		96%

[a] ^{1}H NMR spectral data obtained in C_6D_6 and reported in ppm downfield from tetramethylsilane. Yields determined by ^{1}H NMR of reaction mixtures. [b] Prepared from **2** and 1.0 equiv of RCN. [c] Prepared from **2** and 2.0 equiv of RCN. [d] 1:1 complex not observed under reaction conditions. [e] 2:1 complex formed sluggishly in solution (see text); isolated yield >90%. [f] 1:1 complex is formed in >95% yield in presence of 2 equiv of ^{t}BuCN. [g] Remainder is unreacted **2** (27–50%), which slowly decomposes upon prolonged reaction, and 2:1 complex (16–19%).

coupled with spectral and reactivity studies, strongly suggests the mononuclearity of **4**.

Final confirmation of the molecular structure of compound **4** was obtained through acidolysis. Treatment of **4** with excess dry HCl gas, followed by aqueous workup and ether extraction, afforded a white crystalline solid whose ^{1}H NMR, ^{13}C NMR, IR, and mass spectra and melting point were identical with those of an authentic sample[15] of the expected β-ketoenamine (Scheme I).[28]

Intrigued by this unusual reductive coupling of nitriles and realizing the potential importance of both the intermediate azametallacyclobutene **3** and diazametallacyclohexadiene **4** and of the β-ketoenamine acidolysis products, we have carried out initial exploration of the generality of this reaction sequence. We find that the course of the reaction is critically dependent on the nature of the nitrile employed. Electron rich nitriles led immediately to 2:1 complexes, while electron deficient or sterically hindered nitriles gave comparatively stable 1:1 complexes, with slower conversion to the 2:1 complexes. The results of these studies are summarized in Table I.

From a synthetic standpoint, the β-ketoenamine acidolysis products are well-recognized[16,17] and versatile intermediates for heterocyclic and related syntheses.[18–27] Though a variety of routes to such compounds are known, this unusual reductive coupling of nitriles should serve as a convenient complement, given especially the ease of synthesis of nitriles through simple nucleophilic displacement reactions. We will report our studies of these materials and of intramolecular variants in due course. The metallacyclic products also bear promise for synthetic applications, and we are exploring their follow-up reaction chemistry before removal of the metal. Finally, the electronic effects on 1:1 versus 2:1 complex formation and the surprisingly rapid tautomerization are also being explored.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

---

(15) Prepared by the general procedure of Baraldi et al. (Baraldi, P. G.; Simoni, D; Manfredini, S. *Synthesis* **1983**, 902–903): ^{1}H NMR (C_6D_6) δ 0.91 (s, 9 H, *t*-Bu), 1.24 (s, 9 H, *t*-Bu), 4.8 (br s, 1 H, N*H*), 10.7 (br s, 1H, N*H*); ^{13}C NMR (C_6D_6) δ 28.26 ($C{-}\mathit{C}H_3$), 28.70 ($C{-}\mathit{C}H_3$), 35.85 ($\mathit{C}{-}CH_3$), 42.30 ($\mathit{C}{-}CH_3$), 86.23 ($-CO-\mathit{C}H{=}CH-$), 173.07 ($-CO-CH{=}\mathit{C}H-$), 204.60 ($-\mathit{CO}-CH{=}CH-$); IR ν = 3407 (m, br, N–H), 3346 (m, br, N—H), 2968 (s, C—H), 2928 (m, C—H), 2870 (mw, C═H), 1719 (w), 1634 (m), 1596 (s), 1524 (s) cm^{-1}; MS, *m*/*e* = 183 (9.1), 126 (100); mp 127–129 °C.

(16) Greenhill, J. V. *Chem. Soc. Rev.* **1977**, *6*, 277–294.

(17) Suzuki, K.; Ohkuma, T.; Tsuchihashi, G.-i. *J. Org. Chem.* **1987**, *52*, 2929–2930, and references therein.

(18) Meyers, A. I.; Reine, A. H.; Sircar, J. C.; Singh, S.; Weidman, H.; Fitzpatrick, M. *J. Heterocycl. Chem.* **1968**, *5*, 151–159.

(19) Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Am. Chem. Soc.* **1978**, *100*, 3598–3599.

(20) Barton, D. H. R.; Dressaire, G.; Willis, B. J.; Barrett, A. G. M.; Pfeffer, M. *J. Chem. Soc., Perkin Trans. 1* **1982**, 665–669.

(21) Takeuchi, N.; Okada, N.; Tobinaga, S. *Chem. Pharm. Bull.* **1983**, *31*, 4355–4359.

(22) Leonard, N. J.; Adamcik, J. A. *J. Am. Chem. Soc.* **1959**, *81*, 595–602.

(23) Meyers, A. I.; Singh, S. *Tetrahedron Lett.* **1967**, 5319–5322.

(24) Meyers, A. I.; Reine, A. H.; Gault, R. *J. Org. Chem.* **1969**, *34*, 698–705.

(25) Yoshimoto, M.; Ishida, N.; Hiraoka, T. *Tetrahedron Lett.* **1973**, 39–42.

(26) Abdulla, R. F.; Fuhr, K. H. *J. Org. Chem.* **1978**, *43*, 4248–4250.

(27) Mukaiyama, T.; Ohsumi, T. *Chem. Lett.* **1983**, 875–878.

(28) Typical procedure: Under argon, 0.1 g of **2** (0.362 mmol) in 5 mL of dry benzene (from sodium/benzophenone) was stirred with 80 μL of pivalonitrile (0.724 mmol) for 5.5 h at 50 °C. Removal of solvent in vacuo afforded **4** as a dark red solid in essentially quantitative yield. A solution of **4** (0.1 g, 0.279 mmol) in 9 mL of dry ether (from sodium/benzophenone) was cooled to ca. 0 °C in an ice/salt bath and then treated with an excess of dry HCl gas, immediately precipitating Cp_2TiCl_2. After 10 min, the mixture was opened to air, and 15 mL H_2O was cautiously added. The Cp_2TiCl_2 was removed by filtration, and the filtrate was neutralized with 35 mL of 10% NaOH. The filtrate was extracted twice with ether, affording, after drying ($MgSO_4$) and evaporation of solvent, the β-ketoenamine (47.3 mg, 92%) as a crystalline solid, mp 126–129 °C (authentic sample[15] mp 127–129 °C).

The Gas-Phase Displacement Reaction of Chloride Ion with Methyl Chloride as a Function of Kinetic Energy

Stephan E. Barlow, Jane M. Van Doren, and
Veronica M. Bierbaum*

Department of Chemistry and Biochemistry
University of Colorado
Boulder, Colorado 80309-0215

Received April 21, 1988

Nucleophilic displacement reactions are among the most extensively studied chemical processes in solution[1] and in the gas phase,[2] both by theory[3] and by experiment.[4] The symmetric thermoneutral reactions, for example,

$$^{37}Cl^- + CH_3{}^{35}Cl \rightarrow {}^{35}Cl^- + CH_3{}^{37}Cl \qquad (1)$$

are of central importance in characterizing the potential energy surfaces for these displacement processes, since their reactivity reflects the intrinsic S_N2 barrier in the absence of a thermodynamic driving force. Nevertheless, such thermoneutral substitution reactions have not previously been observed in the gas phase.[5,6]

---

(1) (a) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969. (b) March, J. *Advanced Organic Chemistry*; John Wiley: New York, 1985; Chapter 10 and references therein.

(2) Riveros, J. M.; Josē, S. M.; Takashima, K. *Adv. Phys. Org. Chem.* **1985**, *21*, 197 and references therein.

(3) (a) Dedieu, A.; Veillard, A. *J. Am. Chem. Soc.* **1972**, *94*, 6730. (b) Bader, R. F. W.; Duke, A. J.; Messer, R. R. *J. Am. Chem. Soc.* **1973**, *95*, 7715. (c) Keil, F.; Ahlrichs, R. *J. Am. Chem. Soc.* **1976**, *98*, 4787. (d) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7692, 7694. (e) Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1982**, *104*, 2708. (f) Morokuma, K. *J. Am. Chem. Soc.* **1982**, *104*, 3732. (g) Carrion, F.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 3531. (h) Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 154. (i) Dodd, J. A.; Brauman, J. I. *J. Phys. Chem.* **1986**, *90*, 3559. (j) Evanseck, J. D.; Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1987**, *109*, 2349. (k) Hwang, J.-K.; King, G.; Creighton, S.; Warshel, A. *J. Am. Chem. Soc.* **1988**, *110*, 5297.

(4) (a) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643. (b) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. (c) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959. (d) Hierl, P. M.; Ahrens, A. F.; Henchman, M.; Viggiano, A. A.; Paulson, J. F.; Clary, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 3142.

0002-7863/88/1510-7240$01.50/0

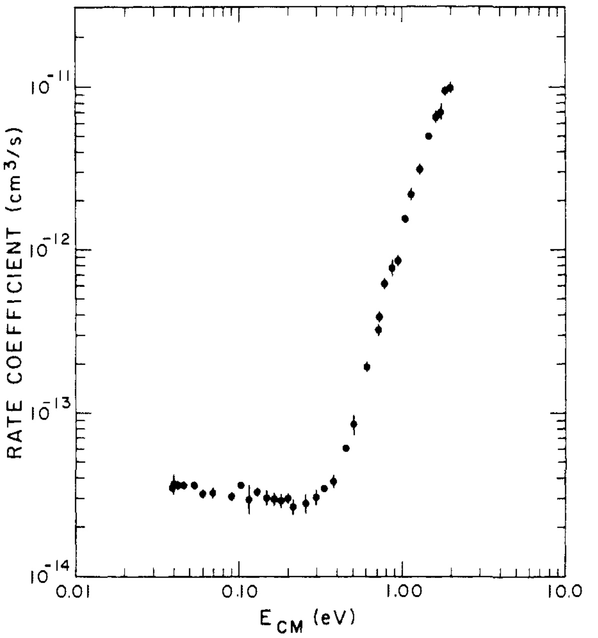


Figure 1. Plot of the rate coefficient for the reaction $^{37}Cl^- + CH_3{}^{35}Cl \rightarrow {}^{35}Cl^- + CH_3{}^{37}Cl$ as a function of the center-of-mass kinetic energy. The lowest energy point corresponds to a thermal energy of 300 K.

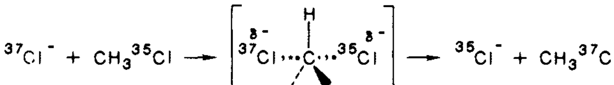
We have now taken advantage of the high sensitivity of our new instrument,[7] together with a modified method of kinetic analysis, to detect the occurrence of this reaction for the first time. We have determined a rate coefficient of 3.5×10^{-14} cm^3 s^{-1} for reaction 1 at 300 K (reaction efficiency = 2×10^{-5}) and report its translational energy dependence up to a center-of-mass kinetic energy of 2 eV. Our data reveal a nearly constant reactivity between 300 K and kinetic energies of about 0.4 eV and uncover a new process leading to isotope exchange at higher kinetic energies.

The experiments were carried out with the tandem Flowing Afterglow-SIFT-Drift instrument which has been described previously.[7] The $^{37}Cl^-$ reactant ion was cleanly injected into the flow-drift tube ($S/N > 3000$, $^{37}Cl^-/^{35}Cl^- \sim 10\,000$), and unenriched methyl chloride was added through a manifold of inlets to initiate the exchange reaction. The $^{37}Cl^-$ and $^{35}Cl^-$ ions were monitored at each reaction distance, and the rate coefficients were evaluated from the normalized conversion of reactant ion.[8] With this method of analysis, ion signals must remain stable only for periods of about 2 min, and mixing and diffusion perturbations are negligible as they are expected to affect both chloride isotopes similarly.

Several experimental checks were made to ensure the reliability of the data. First, the mobility of chloride ion, and thus the drift velocity,[9] was measured as a function of field strength and found to agree with published values[10] within 5%. Addition of large flows of methyl chloride altered these mobilities by less than 2%. Second, addition of sulfur hexafluoride, an excellent electron scavenger,[11] did not affect the results. This eliminates the possibility of collisional detachment of $^{37}Cl^-$, followed by dissociative electron attachment to methyl chloride, as the mechanism of $^{35}Cl^-$ formation. Third, the rate coefficients were found to be independent of reaction distance, indicating that systematic errors due to mixing or turbulence are absent. Finally, the high purity of the methyl chloride was confirmed by GC/MS analysis and titration techniques.[12]

Figure 1 summarizes our rate coefficient measurements as a function of center-of-mass collision energy. A total of 58 experiments was carried out at 36 kinetic energies between 300 K and 2 eV; each experiment consisted of four measurements of the rate coefficient employing different reaction distances. The error bars indicate one standard deviation of the mean of all measurements at a given energy; where no error bars are indicated they are smaller than the data point symbol. Absolute errors are estimated to be ±50%. The rate coefficient for reaction 1 is found to be 3.5×10^{-14} cm^3 s^{-1} at 300 K, corresponding to an efficiency of one reaction in 50 000 collisions; the efficiency for the reverse reaction is identical within our experimental error. Although exceedingly small, this reaction efficiency is a factor of 35 larger than can be accounted for by measured impurities in methyl chloride.[12] The rate coefficient remains nearly constant with increasing kinetic energy up to 0.4 eV and then rises exponentially to 1×10^{-11} cm^3 s^{-1} at 2.0 eV.

The low reactivity at energies below 0.4 eV is in accord with the S_N2 mechanism where carbon undergoes nucleophilic attack by $^{37}Cl^-$ to displace $^{35}Cl^-$ in the entropically unfavorable Walden-inversion process:



$$^{37}Cl^- + CH_3{}^{35}Cl \longrightarrow \left[{}^{37}\overset{\delta-}{Cl}\cdots\overset{H}{C}(H)(H)\cdots{}^{35}\overset{\delta-}{Cl}\right] \longrightarrow {}^{35}Cl^- + CH_3{}^{37}Cl \qquad (2)$$

Modeling of the relatively flat energy dependence of this rate coefficient using a simplified RRKM approach[13] indicates that the transition state lies 1 (±1) kcal/mol above the energy of the reactants. This is in good agreement with the conclusion of Dodd and Brauman[3i] and with the theoretical results of Chandrasekhar et al.[3h] Combining our value of the barrier height with the recently measured complexation energy of $Cl^-{\cdot}CH_3Cl$ (12.2 ± 2 kcal/mol)[14] yields an intrinsic barrier to nucleophilic substitution in reaction 2 of 13.2 ± 2.2 kcal/mol.

The increase in rate coefficient at higher energies corresponds to the onset of a new mechanism for chloride exchange. The exponential rise between 0.5 and 2.0 eV may be fit by the model of translationally driven reactions developed by Chesnavich and Bowers[15-18] from which we find an activation energy of 2.0 eV. We suggest that the mechanism corresponds to anionic attack at chlorine, analogous to that proposed in halogen-metal interconversions.[19] Reaction proceeds through a $[CH_3{\cdot}Cl_2^-]$ intermediate complex in which the chlorine atoms have become equivalent (eq 3):

$$^{37}Cl^- + CH_3{}^{35}Cl \rightleftharpoons [CH_3{\cdot}{}^{35}Cl^{37}Cl^-] \rightarrow {}^{35}Cl^- + CH_3{}^{37}Cl \qquad (3)$$

This complex is expected to lie about 2 eV above the energy of the reactants since production of the separated species, CH_3 +

---

(5) Initial reports (ref 4b) of a rate coefficient measurement for this reaction have been withdrawn (ref 3i), and we have recently determined an upper limit of $k \leq 2 \times 10^{-13}$ cm^3 s^{-1} for reaction 1 with conventional SIFT techniques (ref 6).

(6) Van Doren, J. M.; DePuy, C. H.; Bierbaum, V. M. *J. Phys. Chem.*, in press.

(7) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *81*, 85.

(8) The rate coefficient, k, was determined from the relationship $\ln\{[^{37}Cl^-]/([^{37}Cl^-] + [^{35}Cl^-])\} = -k[CH_3{}^{35}Cl]z/(v_d + v_f)$ where $[CH_3{}^{35}Cl] = 0.758[CH_3Cl]$, z is the reaction distance, and v_d and v_f represent the ion drift and flow velocities, respectively.

(9) McFarland, M.; Albritton, D. L.; Fehsenfeld, F. C.; Ferguson, E. E.; Schmeltekopf, A. L. *J. Chem. Phys.* **1973**, *59*, 6610.

(10) Dotan, I.; Albritton, D. L.; Fehsenfeld, F. C. *J. Chem. Phys.* **1977**, *66*, 2232.

(11) Fehsenfeld, F. C. *J. Chem. Phys.* **1970**, *53*, 2000.

(12) Most of the potential organic impurities in CH_3Cl are expected to be less reactive toward $^{37}Cl^-$ than is CH_3Cl; GC/MS analysis detected no organic contaminants. In contrast, the potential contaminants HCl and Cl_2 are known to be highly reactive (ref 6). Analysis of CH_3Cl by Hauser Laboratories, Boulder, CO, using titration techniques, detected 1.7 ppm HCl and <0.7 ppm Cl_2.

(13) Barlow, S. E.; Van Doren, J. M.; DePuy, C. H.; Bierbaum, V. M.; Dotan, I.; Ferguson, E. E.; Adams, N. G.; Smith, D.; Rowe, B. R.; Marquette, J. B.; Dupeyrat, G.; Durup-Ferguson, M. *J. Chem. Phys.* **1986**, *85*, 3851.

(14) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.

(15) Chesnavich, W. J.; Bowers, M. T. *J. Phys. Chem.* **1979**, *83*, 900.

(16) Theoretical (ref 17) and experimental (ref 18) data indicate that the relative velocity distribution for an atomic ion drifted in helium is Maxwellian. The theory of Chesnavich and Bowers (ref 15) is applied by convolving their translational energy cross section with this energy distribution.

(17) Wannier, G. H. *Bell Syst. Tech.* **1953**, *32*, 170. Whealton, J. H.; Woo, S. B. *Phys. Rev. A* **1971**, *6*, 2319.

(18) Dressler, R. A.; Meyer, H.; Langford, A. O.; Bierbaum, V. M.; Leone, S. R. *J. Chem. Phys.* **1987**, *87*, 5578.

(19) Zefirov, N. S.; Makhon'kov, D. I. *Chem. Rev.* **1982**, *82*, 615.

Cl_2^-, is endothermic by 2.4 eV and an ion-neutral clustering energy of 0.4 eV is reasonable. Further studies of this and other symmetric displacement reactions are currently in progress to explore more fully the nature of the potential energy surfaces for these important processes.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation under Grant CHE-8508629. We are indebted to Professor Charles DePuy for his support and insight throughout this project. We thank Mark Jones for his assistance in the analysis of the methyl chloride, Thuy Dang for her help in data acquisition, and Professor Michael Bowers for valuable discussions.

Electron-Transfer Reactions in the Marcus Inverted Region: Differences in Solvation and Electronic Coupling between Excited Charge-Transfer Complexes and Geminate Radical Ion Pairs

Ian R. Gould,* Roger Moody, and Samir Farid*

Corporate Research Laboratories
Eastman Kodak Company
Rochester, New York 14650-2109

Received June 14, 1988

We have recently shown that the rate constants for return electron transfer within photochemically generated, solvent-penetrated, geminate radical ion pairs ($A^{\bullet-}/D^{\bullet+}$) decrease with increasing exothermicity (the Marcus "inverted region"),[1] which results in widely varying quantum yields for separated ion formation as a function of the energy stored in the radical ion pairs. Radical ions can also be formed by direct excitation in the charge-transfer bands of ground-state donor/acceptor complexes in polar solvents, and there are several reports of reactions via this route,[2] although, in other cases, virtually no free-radical ions are formed.[3,4a] Evidently the yield of free-radical ions from excited CT complexes also varies over a wide range.

Excited CT complexes can be characterized as radical ions at contact distances ($A^{\bullet-}D^{\bullet+}$),[5] which, in polar solvents, yield the solvent-penetrated radical ion pairs ($A^{\bullet-}/D^{\bullet+}$). These intermediates are equivalent to the classical contact and solvent-separated ion pairs. According to Scheme I, energy-wasting return electron transfer reactions within both the excited complex, $(k_{-et})_{ct}$, and the geminate pair, $(k_{-et})_{rip}$, compete with solvent penetration (k_{solv}) and the separation to free-radical ions (k_{sep}). In this communication we report the results of a systematic comparison of the rates of these two electron-transfer reactions, for the same donor/acceptor pairs.

The reaction constants $(k_{-et})_{rip}$ were previously determined for several alkylbenzenes as donors reacting with excited 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) as electron acceptors.[1] Weak CT complexes are formed between TCA and alkylbenzenes with low oxidation potentials.[8]

Scheme I

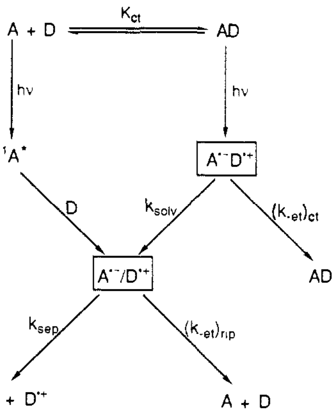
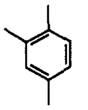
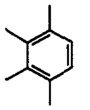
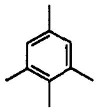
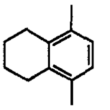
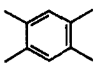
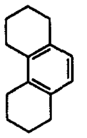
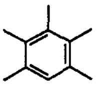
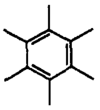


Table I. Quantum Yields of Free Ion Formation and Rate Constants for Return Electron Transfer for Excited CT Complexes (Contact Ion Pairs) and Solvent-Penetrated Ion Pairs of TCA/Benzene Derivatives in Acetonitrile

donor	$(E^{ox})_D - (E^{red})_A$	$(\Phi_{ions})_{ct}$[a]	$(k_{-et})_{ct}$ ($\times 10^{-9}$ s^{-1})	$(\Phi_{ions})_{rip}$[b]	$(k_{-et})_{rip}$[c] ($\times 10^{-9}$ s^{-1})
	2.36	0.0301	0.86	0.056	8.4
	2.28	0.0114	2.68	0.042	11.4
	2.27	0.0103	2.98	0.041	11.7
	2.25	0.0091	3.40	0.040	12.0
	2.22	0.0093	3.41	0.041	11.7
	2.21	0.0074	4.00	0.037	13.0
	2.15	0.0036	8.72	0.035	13.8
	2.03	0.0016	18.12	0.0306	15.8

[a] Quantum yield for formation of free-radical ion formation for photolysis of the CT complexes at 460 nm. [b] Quantum yield for formation of free-radical ions for photolysis of the acceptor at 410 nm, extrapolated to zero concentration of the donor.[1a,9] [c] Calculated assuming $k_{sep} = 5 \times 10^8$ s^{-1}.[1]

---

[1] (a) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 1991. (b) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

[2] (a) Farid, S.; Hartman, S. E.; Evans, T. R. In *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 327. (b) Arnold, D. R.; Wong, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 1894. (c) Wong, P. C.; Arnold, D. R. *Can. J. Chem.* **1980**, *58*, 918. (d) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152. (e) Lewis, F. D.; Simpson, J. T. *J. Phys. Chem.* **1979**, *83*, 2015. (f) Jones, G., II; Haney, W. A.; Phan, X. T. *J. Am. Chem. Soc.* **1988**, *110*, 1922. (g) Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.* **1983**, *105*, 1276. (h) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 2780.

[3] Ledwith, A. In *The Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic Press: New York, 1975; p 209.

[4] (a) Mataga, N.; Shioyama, H.; Kanda, Y. *J. Phys. Chem.* **1987**, *91*, 314. (b) Mataga, N.; Okada, T.; Kanda, Y.; Shioyama, H. *Tetrahedron* **1986**, *42*, 6143.

[5] (a) This theoretical prediction (ref 5b) has been verified experimentally (ref 4, 6, and 7). (b) Mulliken, R. S.; Pearson, W. B. *Molecular Complexes: A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969.

[6] (a) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 1441. (b) Goodman, J. L.; Peters, K. S. *J. Phys. Chem.* **1986**, *90*, 5506. (c) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6459. (d) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 1700.

0002-7863/88/1510-7242$01.50/0 © 1988 American Chemical Society