

Gerhard L. Closs—Contributions to Science

Heinz D. Roth

Department of Chemistry, Rutgers University, New Brunswick, New Jersey, 08855-0939

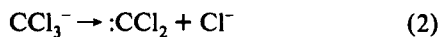
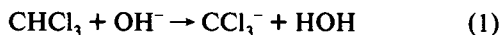
When Gerhard Ludwig Closs passed away on May 24, 1992, the work of one of the great organic chemists came to an untimely end. Professor Closs made significant contributions in four areas: he was an early leader in the field of carbene chemistry, he elaborated various significant aspects of the photosynthetic pigments, he pioneered important applications of magnetic resonance to characterize reaction intermediates, and he elucidated intricate facets of electron-transfer chemistry. This special issue of *The Journal of Physical Chemistry*, dedicated to his memory, provides a welcome opportunity to pay tribute to one of the outstanding chemists of the post-WWII era—and to a friend.

Gerhard Closs was born in Wuppertal-Elberfeld, Germany, on May 1, 1928, and received his elementary education there until he was pressed into military service, as a 16 year old, in 1944. Having survived the ordeal of war and having completed his high school education, he decided on a career in chemistry. He received a Ph.D. in 1955 from Universität Tübingen for work he had done under the direction of Professor Georg Wittig. This work was also the topic of his first publication, "Über Ringerweiterungen und Ringverengerungen durch Ylidumlagerungen."¹ In 1955, he came to the United States and joined R. B. Woodward's group at Harvard for 2 years, working toward the total synthesis of chlorophyll. This work resulted in a 1960 Communication to the Editor in the *Journal of the American Chemical Society*² and in a full paper in *Tetrahedron* 30 years later.³

In 1957, Gerhard Closs joined the University of Chicago as an assistant professor. Given his background, particularly his work with Woodward, it may not be too surprising that he was hired as a natural products chemist. It is an interesting question whether he ever fulfilled the specific expectations of those who hired him. He did publish a paper on tropane deuterio halides⁴ and another on the active constituents of *Panaeolus Venenosus*,⁵ and he continued to work on various aspects of the photosynthetic pigments throughout his career. However, his most significant contributions came in areas unrelated or less directly related to natural products. They can be divided into three different areas, one for each decade of his professional career.

Contributions to Carbene Chemistry

The emerging field of carbene chemistry was the first discipline to which Gerhard Closs was a major independent contributor. Formally, the recorded interest in divalent carbon species dates back to Dumas's attempts to dehydrate methanol;⁶ of course, these experiments were carried out well before the quadrivalence of carbon was recognized. Thus, the actual roots of the carbene field lie in a simple experiment, the base-catalyzed hydrolysis of trichloromethane, which was first carried out and reported by Geuther in 1862.⁷ This experiment was repeated in 1949/50 by Hine, who recognized the ensuing reaction as a new reaction type, an α -elimination, giving rise to dichlorocarbene.⁸



In 1954, Doering and Hoffman trapped the postulated species by addition to cyclohexene, demonstrating its intermolecular reactivity.⁹

The development of divalent-carbon chemistry since these discoveries involved the notion of carbene spin multiplicity,¹⁰ chemical studies probing the reactivity of these intermediates and the stereochemistry of their principal reactions,^{10–12} the correlation between reactivity and spin multiplicity,^{10,13,14} and the application of new physical methods which provided more direct insight into the spin multiplicity and allowed the direct observation of the intermediates.^{15–26} Among these techniques we mention electron paramagnetic resonance (EPR)^{15–17} and electron nuclear double resonance (ENDOR),¹⁷ chemically induced dynamic nuclear polarization (CIDNP),^{18,19} and optical spectroscopy, either in low-temperature glasses²⁰ or in the liquid phase with ever increasing time resolution.^{21–26} Gerhard Closs was at the forefront of these developments and played a significant role in introducing many of these techniques to the study of carbenes.

Closs's first entry into the carbene field involved the generation of a new divalent-carbon compound, chlorocarbene, and its addition to alkenes to generate chlorocyclopropanes.²⁷ When allowed to react with benzene, chlorocarbene gave rise to tropylium chloride;²⁸ the analogous reaction with phenol provided ready access to tropone.²⁹ When the base-induced α -elimination was carried out on chloroalkenes, the resulting alkenylcarbenes formed cyclopropanes via intramolecular cycloadditions.^{30,31} Finally, a cyclopropenylcarbene was investigated as a potential precursor for the then-unknown tricyclo[1.1.0.0.2.4]butane (tetrahedrane) system but, instead, gave rise to a transient cyclobutadiene derivative.³² Additional papers described the generation, reactivity, and stereochemistry of various additional carbenes. Gerhard Closs pioneered the reactions of alkyl and benzal halides with organolithium compounds, all natural extensions of the reactions of Geuther, Hine, and Doering. In the course of these studies, the term "carbenoid" was introduced to denote carbenes that appeared to be complexed with lithium halide.³³

Many of these studies were carried out in collaboration with Lieselotte E. Closs (née Pohmer), Gerhard's wife and, surely, his most productive co-worker—their collaboration resulted in 15 publications between 1959 and 1969. Lieselotte also received a Ph.D. with Georg Wittig for work establishing the transient existence of "dehydrobenzene" (benzyne).^{34,35} She had come to the United States for postdoctoral work at the Massachusetts Institute of Technology. They were married on Aug. 17, 1956, in Cambridge, Massachusetts, a year before the move to Chicago.

Gerhard Closs was granted tenure in 1961 and was promoted to full professor only 2 years later. By the time of the first promotion, he had developed a family of useful reagents that gave him access to interesting products. The nature of these intermediates and their mode of reaction were derived from the structure and stereochemistry of the isolated reaction products, applying carefully selected mechanistic criteria. These studies were carried out with state-of-the-art methodologies and gave rise to noteworthy results. Yet, they did not satisfy Gerhard Closs. He asked reaching questions; he needed to know more about the divalent intermediates. He wanted to characterize them more thoroughly and, possibly, observe them directly.

By 1962 he had decided that electron spin resonance might hold the key to the structure of carbenes, and he selected diphenylmethylene as his first target. He used benzophenone as a single crystal host for diphenyldiazomethane, from which diphenylcarbene was generated by photolysis at cryogenic temperatures. In collaboration with Clyde Hutchison, an ex-

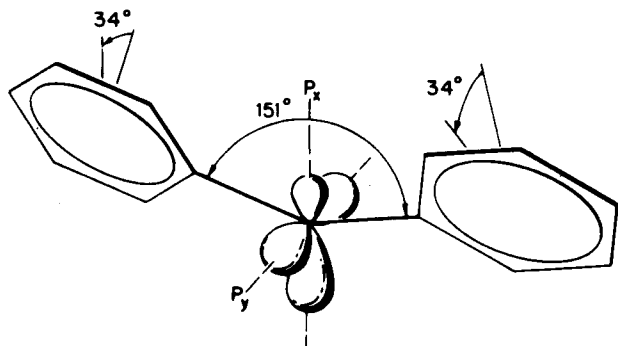
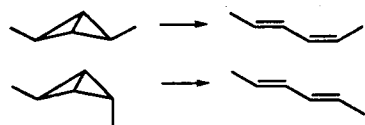


Figure 1. Structure of diphenylmethylene as established by the ENDOR experiments of Doetschman and Hutchison.¹⁷

perienced ESR spectroscopist, he observed the first ESR spectrum of a ground-state triplet carbene in a single crystal.¹⁶ About 2 weeks before the Chicago group observed their first results, the identical species was generated in a glassy matrix at Bell Laboratories.¹⁵ However, the single crystal results of the Chicago collaborators lent themselves more readily to analysis and interpretation. Ultimately, with the help of electron nuclear double resonance, these results revealed the detailed structure of this intermediate (Figure 1).¹⁷

Gerhard Closs also pioneered the application of additional physical methods to carbene chemistry, particularly time-resolved optical spectroscopy²² and chemically induced dynamic nuclear polarization.¹⁸ The relative rates of various carbene reactions had been determined since the mid-1950s, for example, by Skell and Garner³⁶ as well as by Doering and Henderson.³⁷ Only one isolated study had dealt with the application of time-resolved optical spectroscopy to carbene chemistry²¹ when Closs studied the rate of addition of diphenylmethylene to various alkenes by this technique,^{22,38} opening the field to the many studies that were to follow.^{23–26} Similarly, the first applications of the CIDNP technique to carbene chemistry was carried out in Closs's laboratory (*vide infra*),¹⁸ breaking ground for the subsequent studies of others.^{19,39–41}

Various aspects of carbene chemistry remained the primary topic of Closs's work for the first decade of his scientific career. Of his first 50 publications, more than 30 dealt with carbenes or carbenoids and several others with the characterization of cyclopropanes and bicyclobutanes which had become available by his carbene reactions. Among these studies, we mention the isomerization of 2,4-dimethylbicyclo[1.1.0]butane to butadiene. The conservation of orbital symmetry, a concept developed by Woodward and Hoffmann in the early 1960s,⁴² requires that this reaction proceed as a concerted [$\sigma^2_s + \sigma^2_a$] process with predictable consequences for the stereochemical fate of the migrating carbon centers. The decisive experiment in favor of the orbital symmetry controlled ring opening was provided by Closs and Pfeffer, who delineated the rearrangement of *endo,exo*- and *exo,exo*-2,4-dimethylbicyclobutane to *E,E*- and *E,Z*-hexadiene, respectively.⁴³



Closs's successful excursion into the ESR spectroscopy of triplets spawned other efforts, such as the study of fluorenylidene.⁴⁴ It led to the detection of triplet carbenes by optical spectroscopy,⁴⁵ including the microsecond time-resolved study of diphenylmethylene.²² Additional EPR studies described interesting diradicals, including several species related to benzocyclopropanes⁴⁶ and some intermediates generated by addition of triplet carbenes to alkenes,⁴⁷ and he was the first to observe and

characterize cyclopentadienyl.⁴⁸ Additional highly significant EPR studies were carried out in the final decade of his life.

Contributions to Chemically Induced Nuclear Spin Polarization

By the mid-1960s, Gerhard Closs had become an acknowledged expert in the carbene field. At this time, several reports appeared in the chemical literature describing various chemical reactions leading to nuclear magnetic resonance emission.^{49–51} Since some of the reactions were known to involve free radicals, the observed effects were originally explained as electron–nuclear cross relaxation phenomena, hence the term “chemically induced dynamic nuclear polarization” (CIDNP) for the new phenomenon.^{50,52} However, the cross relaxation mechanism was soon found wanting, as an increasing number of effects became known that were incompatible with the cross relaxation mechanism.^{18,49,50,53,54} Clearly, a more appropriate theory was needed, and Gerhard Closs, with his unsurpassed understanding of organic reaction mechanisms and his rigorous expertise in magnetic resonance, was in a unique position to solve the puzzle posed by the CIDNP phenomenon.

Closs entered the CIDNP field with all his considerable vigor. In 1969 four back-to-back Communications appeared in the *Journal of the American Chemical Society*,^{18,54–56} followed by six more for a total of 10 Communications in only 20 months. After two preliminary publications describing the effects observed in photoreactions of diphenyldiazomethane¹⁸ and benzophenone,⁵⁴ he was able to eliminate the Overhauser mechanism.⁵⁵ He also addressed several later claims of this mechanism^{57–59} and refuted them decisively.^{60,61} Although a special variation of the Overhauser mechanism has been established in a few systems involving the electron-transfer reactions of triplet ketones,^{62,63} it is clear that this mechanism is a rare exception, rather than the rule.

Having eliminated the cross relaxation mechanism, Gerhard Closs began to probe the real origin of the spin polarization effects. He recognized that all CIDNP effects required the involvement of radical pairs,⁵⁵ and he developed the underlying theory based on elegantly designed experiments.^{56,64–67} Specifically, he was able to show that the effects reflected the spin multiplicity (μ) of the precursor from which the pair was generated and suggested CIDNP “as a tool for determination of spin multiplicities of radical pair precursors.”⁵⁶ He also recognized, and demonstrated, that the polarization pattern of CIDNP effects depends critically on the relative g factors (Δg) of the paired radicals (Figure 2).⁶⁵

At the time when Closs and his group were working on this project, Oosterhoff and Kaptein in Leiden also considered the theory and demonstrated additional elements of it. The Leiden group noted the “dependence of the polarization upon type of reaction”: in-cage combination products and cage-escape (free radical) products were found to show the opposite polarization.⁵³ They also found that protons with hyperfine coupling constants (hfc 's) of opposite sign will have opposite signal directions;⁵³ for example, in products derived from ethyl radical the α - and β -protons (negative and positive hfc 's, respectively) were found to show the opposite polarization.⁵³ The theory resulting from the work of the Chicago and Leiden groups (“Radical Pair Theory”) is now generally accepted and can explain the vast majority of all nuclear spin polarization effects.^{68–71} Occasionally, the term CKO (Closs, Kaptein, Oosterhoff) theory is used in tribute to the major contributors.

More than 20 additional publications dealing with the application of CIDNP and with the elucidation of additional facets followed. Closs and his collaborators made significant contributions to the understanding of biradicals.^{48,72–76} For example, the magnetic field dependence of the CIDNP effects observed for a series of biradicals yielded their average singlet–triplet splitting⁷⁵ as well as the biradical lifetimes (Figure 3).⁷⁶ In the course of these studies, 1,3-cyclopentadienyl was recognized as

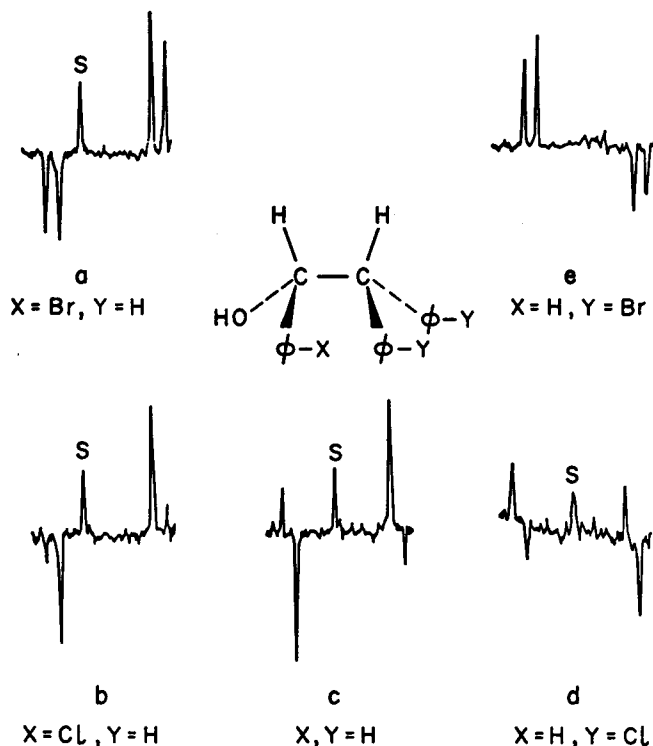


Figure 2. CIDNP spectra (benzylic protons) of coupling products generated following the photoreaction of benzaldehydes in the presence of diphenylmethanes.⁶⁵

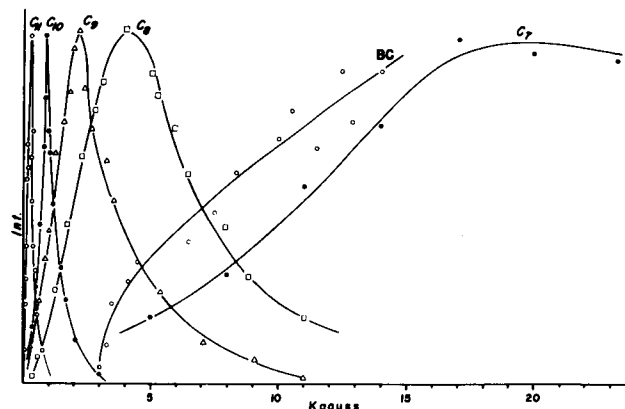


Figure 3. Normalized intensity vs field curves of aldehyde proton signals obtained on photolysis of cycloalkanones and a bicyclic ketone (BC). All signals are in emission.⁷⁶

"a localized 1,3 carbon diradical with a triplet ground state" by the combined application of CIDNP and EPR.⁴⁸ Closs and colleagues also treated relaxation and cross relaxational phenomena (CIDNP pumped NOE).^{77,78} They established both scalar and dipolar contributions to cross relaxation, which give rise to either the same polarization phase or the opposite one in a nucleus which does not interact with the unpaired electron spin. These experiments demonstrated an important limitation to the interpretation of CIDNP results, particularly in experiments designed to delineate the electronic structures of reactive intermediates (e.g., radical cations)⁷⁹ based on the polarization patterns of their reaction products.

Closs also pioneered flash photolysis with CIDNP detection, a technique that combines the advantages of time-resolved laser spectroscopy with the structural information content unique to CIDNP.⁸⁰⁻⁸⁶ "The basis for the success of the time-resolved method is the fact that geminate processes are complete in a fraction of a microsecond, while combination of free ions and/or exchange ... may take tens or hundreds of microseconds depending on concentration."⁸¹ This method has been adopted

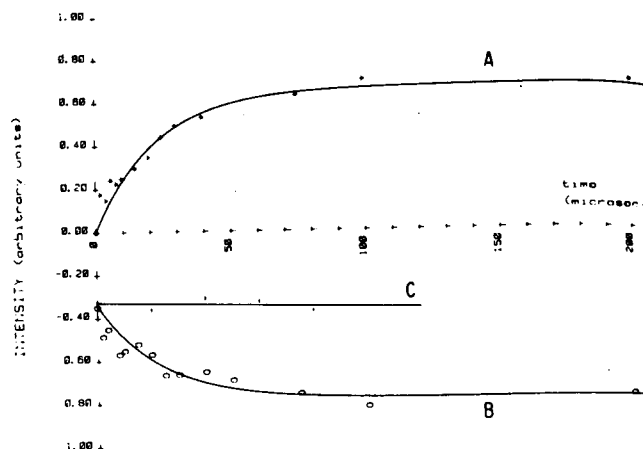


Figure 4. Normalized line intensities of bibenzyl (A) and deoxybenzoin (B) observed during the photolysis of deoxybenzoin as a function of delay time τ . The deoxybenzoin polarization in the presence of a (thiol) free radical scavenger is designated C.⁹²

in several laboratories for a range of applications.⁸⁷⁻⁹⁰ In Closs's own laboratory this technique was applied successfully to such diverse areas as determining the relative hyperfine coupling constants of radical ions of chlorophylls and derivatives⁸¹ and probing the kinetics of triplet states and biradicals.⁸⁰ In the former experiment, CIDNP effects are generated by a photoinduced electron-transfer reaction; the observed intensities at a delay time of 1 μ s yield signs and a relative magnitude of hyperfine coupling constants in good agreement with ENDOR results.^{91,92} The second experiment to be mentioned here involves the light-induced α -cleavage of deoxybenzoin. The reactant can be regenerated either by geminate recombination of the resulting radical pair, or, accompanied by bibenzyl, by combination of uncorrelated pairs. At the shortest delay attainable at that time (1 μ s) the reactant shows the expected geminate polarization; upon increasing the delay time to 100 μ s, this signal grows due to the free radical combination (Figure 4).

In the last decade of his life, Gerhard Closs became interested in several aspects of chemically induced dynamic electron polarization (CIDEP), a phenomenon related to CIDNP and discovered several years before the first CIDNP effects.⁹³ Essentially all electron spin polarization effects observed in the 20 years following the initial discovery could be explained logically either by the radical pair or the triplet mechanism or by a combination of both.^{94,95} In the mid-1980s, several time-resolved CIDEP spectra with highly unusual features were observed upon photolysis of ketones in micelles.^{96,97} The unusual appearance of these spectra could not be explained adequately by any of the existing theories. Gerhard Closs took an interest in these effects and in collaboration with M. Forbes and J. Norris investigated similar systems.⁹⁸ The unusual effects were recognized as manifestations of electron spin-spin interactions which are rapidly lost in solution but "remain observable because of limited diffusion in micelles".⁹⁸ A similar explanation was offered independently by McLauchlan and co-workers.⁹⁹ The concept of "spin-correlated radical pairs" is now generally accepted, and this memorial volume contains several papers describing such spectra. More recently, the time-resolved EPR method was applied to electron spin polarized biradicals in solution, a natural extension of Closs's earlier work on biradicals.¹⁰⁰⁻¹⁰² The shape and time dependence of the CIDEP spectra of acyl-alkyl as well as alkyl-alkyl polymethylene biradicals can be simulated using a perturbation theory approximation, yielding the electron spin-spin interaction, J , and the end-to-end contact rate, which is inversely related to the lifetime. In characteristic fashion, the papers contain the outline of how many as yet unanswered questions were to be approached. These elegant studies represent the culmination of

Closs's ESR studies; remarkably, Gerhard Closs was still breaking new ground at the onset of the seventh decade of his life.

There can be no doubt that Gerhard Closs's significant contributions have been instrumental in making the CIDNP method a well-defined, sophisticated, powerful and reliable technique with a broad spectrum of important applications; his contributions to CIDEP were left unfinished. It is interesting to note that the young assistant professor was assigned supervision of the departmental NMR instrument when he first came to Chicago. Surely, Gerhard Closs made the most of the opportunities this position offered.

Electron Transfer and the Marcus Inverted Region

In 1979 Gerhard Closs accepted the position of a section head in the Chemistry Division at Argonne National Laboratory. He kept this position for but three years, most likely because he was not an enthusiastic administrator. Nevertheless, this appointment was to influence significantly the direction of his research in the final decade of his life. At Argonne he began to collaborate with Jim Norris on a variety of problems in the general area of EPR; this collaboration yielded nine papers over the next 12 years, among them the above-mentioned theory of spin-correlated radical pairs,⁹⁸ an elegant study of the structure and dynamics of the trimethylcyclopropenyl radical,¹⁰³ and several significant contributions to the understanding of primary states of bacterial photosynthesis.^{104–107}

He also began to take an interest in the electron-transfer work of John Miller, who had accumulated evidence for the existence of the "Marcus inverted region". Over 3 decades ago, Marcus formulated the rate of an electron-transfer reaction as a function of two parameters, its driving force, the free energy, ΔG° and a "solvent reorganization energy", λ_s , required to accommodate the changing charge distribution.^{108,109}

$$k_{ET} = A' \exp[-(\Delta G^\circ + \lambda_s)^2 / (4\lambda_s k_B T)]$$

The most striking conclusion emerging from this work was the prediction that electron-transfer rates increase with increasing driving force to a maximum, at $\lambda_s = \Delta G^\circ$, but then unexpectedly (and perhaps counterintuitively) decrease upon further increases in driving force. The essential predictions of this theory were reproduced by many theoretical approaches descending from the original idea of Marcus.¹¹⁰ It took almost 30 years before this prediction was finally confirmed by experiment.

John Miller had studied intermolecular electron transfer between randomly distributed entities in rigid glasses.¹¹¹ The results were quite interesting but the data difficult to interpret. In the collaboration that ensued and continued until Professor Closs's death, donor and acceptor were linked by a rigid steroid spacer, allowing the study of intramolecular electron transfer at a known distance. The results were the first to demonstrate unambiguously the existence of the Marcus inverted region. Less than five months after Gerhard Closs's death, R. A. Marcus was awarded the 1992 Nobel Prize in chemistry. In the announcement, the Swedish Academy pointed out that the Nobel Committee had long recognized the significance of Marcus's theory but had waited for experimental verification before awarding the prize.

Electron-transfer reactions had failed to reveal any evidence for an "inverted" region in spite of detailed investigations.^{112,113} The first indication for any reduction of the electron-transfer rate with increasing driving force was observed by Miller and co-workers in the (charge neutral) electron transfer from radiolytically generated radical anions to aromatic hydrocarbons in frozen solutions.¹¹¹ These reactions covered free energy changes ranging from $-\Delta G^\circ = 0.01$ to 2.75 eV; the rates of electron transfer were found to decrease at high exothermicities.¹¹¹

The analysis of these data is based on a random distance distribution between donor and acceptor, an assumption that cannot be confirmed readily. Gerhard Closs noted that any

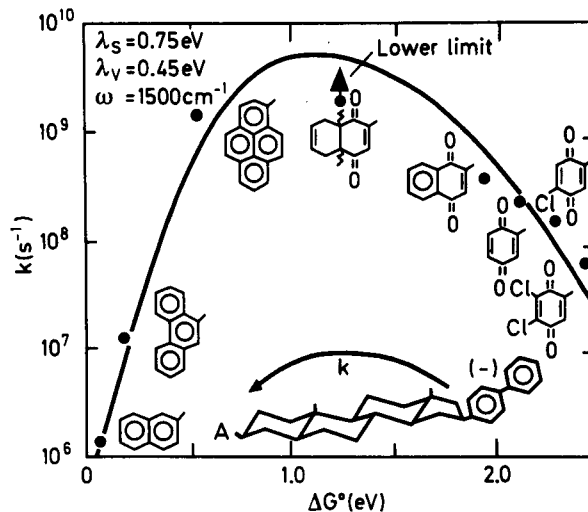


Figure 5. Intramolecular rate constants as a function of free energy change in 2-methyloxacyclopentane solution at 296 K. The electron transfer occurs from biphenyl anions to the eight different acceptor moieties (shown adjacent to the data points), in eight bifunctional molecules of the general structure shown in the center.¹¹⁴

ambiguities due to the random distribution could be removed if intramolecular electron transfer were studied in a series of molecules of the general type A–Sp–B, in which two potential acceptors are linked by the rigid 5 α -androstan skeleton. The electron-transfer rates observed for the radiolytically generated monoanions of these systems showed a striking deviation from the classical Brønsted relationship (Figure 5)^{114,115} and confirm unambiguously the predictions of Marcus.^{108,109} The original confirmation of the inverted Marcus region in a charge-exchange reaction^{114,115} stimulated other groups to investigate other systems, leading to the discovery of inverted Marcus behavior in several charge recombination reactions^{116–118} and possibly even in a charge separation process.¹¹⁹

The continued collaboration between Miller and Closs in the electron-transfer field produced many additional significant results: they established the nonlinear dependence of electron-transfer rates upon solvent polarity,¹¹⁴ they probed the distance dependence using decalin and cyclohexane spacers,^{120,121} and they probed the temperature dependence as a function of driving force¹²² and documented the temperature independence of electron-transfer rates in the inverted Marcus region.¹²³ Having studied both "hole"- and electron-transfer rates, it occurred to Closs that triplet energy transfer could be considered the sum of the two processes. This consideration spawned an illuminating, unprecedented comparison of the rates of hole, electron, and triplet energy transfer (Figure 6).^{124–126} The extensive electron-transfer work in Closs's laboratory suggested that donor and acceptor are coupled via interactions with the orbitals of the intervening molecular fragments (superexchange). This may very well have stimulated Gerhard Closs to reconsider this type of interaction in biradicals, as mentioned earlier.

Conclusion

The work of Gerhard Closs has found wide recognition both at the University of Chicago and in the scientific community at large. At Chicago, he was appointed the Michelson Distinguished Service Professor, and his colleagues honored him along with N.C. Yang with a symposium on the occasion of their 60th birthdays. He was awarded the Jean Servas Stas Metal of the Belgian Chemical Society, he won the James Flack Norris Award and the A.C. Cope Award of the American Chemical Society, he was awarded the Photochemistry Prize of the Inter-American Photochemical Society (I-APS), and he was elected a member of the National Academy of Sciences and the National Academy

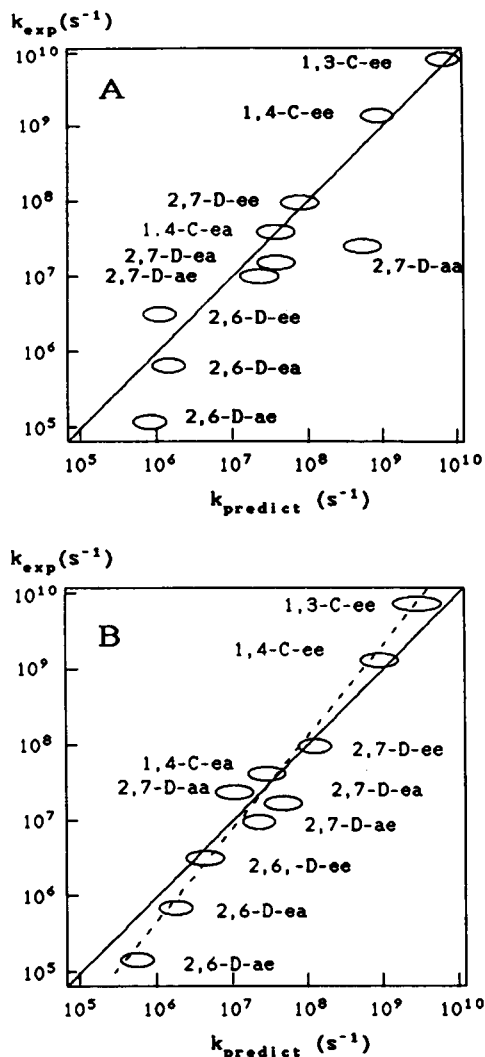


Figure 6. Experimental triplet-transfer rate constants plotted against rate constants predicted from electron- and hole-transfer rates. Solid line: perfect fit to the correlation equation; dotted line, least-squares fit of points. Ellipses represent the estimated uncertainties. Note that the estimated rate constants contain the cumulative error of two measurements.¹²⁴

of Arts and Sciences. In honoring the memory of G. L. Closs, the I-APS has instituted a Gerhard L. Closs Memorial Award, allowing a student to attend the I-APS Winter Meeting.

Gerhard Closs also was honored as chairman of the Gordon Research Conferences on Free Radical Reactions and on Radical Ions, as well as by numerous distinguished lectureships, in several European countries, Canada, and the United States. This included the Bayer Lectureship at Universität Köln, where the author first met him; a visiting professorship at Yale, where the acquaintance was renewed; regular visits to (AT&T) Bell Laboratories; and the Merck Distinguished Lectureship at Rutgers University, where the author was privileged to be his host.

Professor Closs was a featured speaker at many national and international congresses and symposia. Indeed, his participation at meetings may well have been one of his most important contributions to science. He brought to these meetings a keen analytical mind and the command of an unequalled breadth of chemical topics, ranging from the subtlest details of organic synthesis to the intricacies of chemical physics. This combination allowed him to probe proposed theories or mechanistic interpretations, as they were being presented. Few of his peers made more pertinent comments than Gerhard did, and few could offer their comments in more impertinent fashion, when he felt it appropriate. Even experienced and accomplished lecturers must have felt at least a tinge of apprehension when he raised his hand

in his characteristic fashion and, upon being recognized, uttered his familiar "I would like to take issue with ...". The presence of Gerhard Closs in the audience kept many a speaker "honest".

Gerhard Closs relaxed by sailing, sometimes racing his boat on Lake Michigan for hours, days, or even weeks. He also enjoyed the arts: he relished his fine collection of graphic art, having acquired many pieces on his worldwide travels. He was stimulated by theater performances, including modern plays and the avant-garde, and he enjoyed classical music. However, he never allowed himself to be persuaded to attend an opera performance, having sworn off opera following a performance of daPonte and Mozart's *Così Fan Tutte* in Wuppertal in the early 1940s.

With the death of Gerhard Closs, the chemical sciences have lost one of their most formidable champions, a practitioner of the highest intellectual standards, a keen mind, and a skilled experimenter, unsurpassed in combining experiment and theory to illuminate a problem, always probing accepted theories and never afraid to break new ground. The scientific community mourns a teacher, mentor, collaborator, and kindred spirit. A few, who were privileged, mourn a friend.

References and Notes

- (1) Wittig, G.; Mindermann, F.; Closs, G. L. *Liebigs Ann. Chem.* **1955**, 594, 89–118.
- (2) Woodward, R. B.; Ayer, W. A.; Beaton, J. M.; Bickelhaupt, F.; Bonnett, R.; Buchschacher, P.; Closs, G. L.; Dutler, H.; Hannah, J.; Hauck, F. P.; Itô, S.; Langemann, A.; Le Goff, E.; Leimgruber, W.; Lwowski, W.; Sauer, J.; Valenta, Z.; Volz, H. *J. Am. Chem. Soc.* **1960**, 82, 3800–3802.
- (3) Woodward, R. B.; Ayer, W. A.; Beaton, J. M.; Bickelhaupt, F.; Bonnett, R.; Buchschacher, P.; Closs, G. L.; Dutler, H.; Hannah, J.; Hauck, F. P.; Itô, S.; Langemann, A.; Le Goff, E.; Leimgruber, W.; Lwowski, W.; Sauer, J.; Valenta, Z.; Volz, H. *Tetrahedron* **1990**, 46, 7599–7659.
- (4) Closs, G. L. *J. Am. Chem. Soc.* **1959**, 81, 5456–5461.
- (5) Closs, G. L.; Gable, N. W. *Mycologia XI* **1959**, 211.
- (6) Dumas, J. B. *Ann. Chim. Phys.* [2] **1835**, 28.
- (7) Geuther, A. *Liebigs Ann. Chem.* **1862**, 123, 121.
- (8) Hine, J. *J. Am. Chem. Soc.* **1950**, 72, 2438.
- (9) Doering, W. von E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, 76, 2162.
- (10) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, 78, 4496; **1959**, 81, 3383.
- (11) Doering, W. von E.; LaFlamme, P. J. *J. Am. Chem. Soc.* **1956**, 78, 5447.
- (12) Doering, W. von E.; Prinzbach, H. *Tetrahedron* **1959**, 6, 24.
- (13) DeMore, W. B.; Benson, S. W. *Adv. Photochem.* **1964**, 2, 217.
- (14) Gaspar, P. P.; Hammond, G. S. In *Carbene Chemistry*; Kirmse, W., Ed.; Academic Press: New York, 1964; p 235.
- (15) Murray, R. W.; Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, 84, 3213.
- (16) Brandon, R. W.; Closs, G. L.; Hutchison, C. A., Jr. *J. Chem. Phys.* **1962**, 37, 1878.
- (17) Doetschman, D. C.; Hutchison, C. A., Jr. *J. Chem. Phys.* **1972**, 56, 3964.
- (18) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1969**, 91, 4549–4550.
- (19) Roth, H. D. *Acc. Chem. Res.* **1977**, 10, 85.
- (20) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, 1, 339.
- (21) Moritani, I.; Murahashi, S. I.; Ashtaka, H.; Kimura, K.; Tsubomura, H. *J. Am. Chem. Soc.* **1968**, 90, 5918.
- (22) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, 98, 8190.
- (23) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, 102, 5958.
- (24) Eisenthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; DuPuy, C.; Heffernon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980**, 102, 6563.
- (25) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, 102, 7576.
- (26) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, 104, 6813.
- (27) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1959**, 81, 4996–4997.
- (28) Closs, G. L.; Closs, L. E. *Tetrahedron Lett.* **1960**, 10, 38–40.
- (29) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1961**, 83, 599–602.
- (30) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1961**, 83, 1003–1004.
- (31) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1961**, 83, 2015–2016.
- (32) Closs, G. L.; Rao, V. N. M. *J. Am. Chem. Soc.* **1966**, 88, 4116–4117.
- (33) Closs, G. L.; Moss, R. A.; Coyle, J. J. *J. Am. Chem. Soc.* **1962**, 84, 4985–4986.
- (34) Wittig, G.; Pohmer, L. *Angew. Chem.* **1955**, 67, 348.
- (35) Wittig, G.; Pohmer, L. *Chem. Ber.* **1956**, 89, 1334–1351.
- (36) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, 78, 5430.
- (37) Doering, W. von E.; Henderson, W. A., Jr. *J. Am. Chem. Soc.* **1958**, 80, 5274.
- (38) Closs, G. L. In *Carbenes*; Moss, R. A.; Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 159–183.

- (39) Cocivera, M.; Roth, H. D. *J. Am. Chem. Soc.* **1969**, *91*, 2573–2574.
- (40) Iwamura, H.; Imahashi, Y.; Kushida, K. *J. Am. Chem. Soc.* **1974**, *96*, 921. Iwamura, H.; Imahashi, Y.; Oki, M.; Kushida, K.; Satoh, S. *Chem. Lett.* **1974**, 259.
- (41) Bethel, D.; Hayes, J.; Newall, A. R. *J. Chem. Soc. Perkin Trans. 2* **1974**, 1307.
- (42) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1971.
- (43) Closs, G. L.; Pfeffer, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2452.
- (44) Brandon, R. W.; Closs, G. L.; Davoust, C. E.; Hutchison, C. A., Jr.; Kohler, B. E.; Silbey, R. J. *Chem. Phys.* **1965**, *43*, 2006–2016.
- (45) Closs, G. L.; Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1966**, *44*, 413–414.
- (46) Closs, G. L.; Kaplan, L. R.; Bendall, V. I. *J. Am. Chem. Soc.* **1967**, *89*, 3376–3377.
- (47) Closs, G. L.; Kaplan, L. R. *J. Am. Chem. Soc.* **1969**, *91*, 2168.
- (48) Closs, G. L.; Buchwalter, S. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857–3858.
- (49) Bargon, J.; Fischer, H.; Johnson, U. Z. *Naturforsch. A* **1967**, *22*, 1551.
- (50) Ward, H. R.; Lawler, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 5518.
- (51) Bargon, J.; Fischer, H. Z. *Naturforsch. A* **1967**, *22*, 1556.
- (52) Lawler, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 5519.
- (53) Kaptein, R. *Chem. Phys. Lett.* **1968**, *2*, 261.
- (54) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1969**, *91*, 4550–4552.
- (55) Closs, G. L. *J. Am. Chem. Soc.* **1969**, *91*, 4552–4554.
- (56) Closs, G. L.; Trifunac, A. D. *J. Am. Chem. Soc.* **1969**, *91*, 4554–4555.
- (57) Adrian, F. *Chem. Phys. Lett.* **1974**, *26*, 437–439.
- (58) Choo, K. Y.; Wan, J. K. S. *J. Am. Chem. Soc.* **1975**, *97*, 7127.
- (59) Wan, J. K. S.; Elliott, A. J. *Acc. Chem. Res.* **1977**, *10*, 161.
- (60) Closs, G. L. *Chem. Phys. Lett.* **1975**, *32*, 277–278.
- (61) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3483–3490.
- (62) Roth, H. D.; Schilling, M. L. M.; Hutton, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 7792–7799.
- (63) Roth, H. D.; Hutton, R. S.; Schilling, M. L. M. *Rev. Chem. Intermed.* **1979**, *3*, 169–195.
- (64) Closs, G. L.; Trifunac, A. D. *J. Am. Chem. Soc.* **1970**, *92*, 2183–2184.
- (65) Closs, G. L.; Doubleday, C. E.; Paulson, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 2185–2186.
- (66) Closs, G. L.; Trifunac, A. D. *J. Am. Chem. Soc.* **1970**, *92*, 2186–2187.
- (67) Closs, G. L.; Trifunac, A. D. *J. Am. Chem. Soc.* **1970**, *92*, 7227–7229.
- (68) Closs, G. L. *Adv. Magn. Reson.* **1974**, *7*, 157.
- (69) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251, 6262.
- (70) Adrian, F. J. *J. Chem. Phys.* **1970**, *53*, 3374; **1971**, *54*, 3912, 3918.
- (71) Freed, J. H.; Pedersen, J. B. *Adv. Magn. Reson.* **1976**, *8*, 1.
- (72) Closs, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 1546–1547.
- (73) Closs, G. L. *Ind. Chim. Belg.* **1971**, *36*, 1064.
- (74) Closs, G. L.; Doubleday, C. E. *J. Am. Chem. Soc.* **1972**, *94*, 9248–9249.
- (75) Closs, G. L.; Doubleday, C. E. *J. Am. Chem. Soc.* **1973**, *95*, 2735–2736.
- (76) Closs, G. L. In *Chemically Induced Magnetic Polarization: Theory, Technique, and Applications*; NATO Advanced Study Institutes Series C, Vol. 34; Muus, L. T., Atkins, P. W., McLauchlan, K. A., Pedersen, J. B., Eds.; D. Reidel: Dordrecht-Holland, 1977; Chapter XIII, pp 225–256.
- (77) Closs, G. L.; Czeropski, M. S. *Chem. Phys. Lett.* **1977**, *45*, 115–116.
- (78) Closs, G. L.; Czeropski, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6127–6128.
- (79) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343–350.
- (80) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 1639–1641.
- (81) Closs, G. L.; Sitzmann, E. V. *J. Am. Chem. Soc.* **1981**, *103*, 3217–3219.
- (82) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3586–3588.
- (83) Closs, G. L.; Miller, R. J. *Rev. Sci. Instrum.* **1981**, *52*, 1876–1885.
- (84) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 4543–4544.
- (85) Closs, G. L.; Miller, R. J.; Redwine, O. D. *Acc. Chem. Res.* **1985**, *18*, 196–202.
- (86) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 6131–6133.
- (87) Hore, P. J.; Zuiderweg, E. R. P.; Kaptein, R.; Dijkstra, K. *Chem. Phys. Lett.* **1981**, *83*, 376.
- (88) Turro, N. J.; Zimmt, M. B.; Gould, I. R. *J. Am. Chem. Soc.* **1983**, *105*, 6347.
- (89) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 6098–6099.
- (90) Goetz, M. *Chem. Phys. Lett.* **1990**, *147*, 143–154.
- (91) Scheer, H.; Katz, J. J.; Norris, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1372.
- (92) Borg, D. C.; Forman, J.; Fajer, J. *J. Am. Chem. Soc.* **1976**, *98*, 6889.
- (93) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.
- (94) *Spin Polarization and Magnetic Effects in Radical Reactions*; Molin, Yu. N., Ed.; Elsevier: Amsterdam, 1984; Chapters 2, 4, 8.
- (95) *Chemically Induced Magnetic Polarization: Theory, Technique, and Applications*; NATO Advanced Study Institutes Series C, Vol. 34; Muus, L. T., Atkins, P. W., McLauchlan, K. A., Pedersen, J. B., Eds.; D. Reidel: Dordrecht-Holland, 1977; Chapters V–IX, XI, XIX.
- (96) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. *J. Chem. Phys. Lett.* **1984**, *110*, 275. Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J.; Mochida, K. *Chem. Phys. Lett.* **1985**, *120*, 401.
- (97) Murai, H.; Sakaguchi, Y.; Hayashi, H.; I'Haya, Y. *J. Phys. Chem.* **1986**, *90*, 113.
- (98) Closs, G. L.; Forbes, M. D. E.; Norris, J. R., Jr. *J. Phys. Chem.* **1987**, *91*, 3592–3599.
- (99) Buckley, C. D.; Hunter, D. A.; Hore, P. J.; McLauchlan, K. A. *Chem. Phys. Lett.* **1987**, *135*, 307.
- (100) Closs, G. L.; Forbes, M. D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6185–6187.
- (101) Closs, G. L.; Forbes, M. D. E. *J. Phys. Chem.* **1991**, 1924–1933.
- (102) Closs, G. L.; Forbes, M. D. E.; Piotrowiak, P. *J. Am. Chem. Soc.* **1992**, *114*, 3285–3294.
- (103) Closs, G. L.; Evanochko, W. T.; Norris, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 350–352.
- (104) Bowman, M. K.; Budil, D. E.; Closs, G. L.; Kostka, A. G.; Wraight, C. A.; Norris, J. R. *Proc. Natl. Acad. Sci. USA* **1981**, *78*, 3305–3307.
- (105) Norris, J. R.; Bowman, M. K.; Budil, D. E.; Tang, J.; Wraight, C. A.; Closs, G. L. *Proc. Natl. Acad. Sci. USA* **1982**, *79*, 5532–5536.
- (106) Gonen, O.; Regev, A.; Levanon, H.; Thurnauer, M. C.; Norris, J. R.; Closs, G. L. *Chem. Phys. Lett.* **1985**, *113*, 117–122.
- (107) Gast, P.; Gottschalk, A., Jr.; Norris, J. R.; Closs, G. L. *FEBS Lett.* **1989**, *243*, 1.
- (108) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
- (109) Marcus, R. A. *Can. J. Chem.* **1959**, *37*, 155.
- (110) For an extensive list of references to electron transfer theories see reference 111.
- (111) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057.
- (112) Rehm, D.; Weller, A. *Israel J. Chem.* **1970**, *8*, 259.
- (113) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2909.
- (114) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.
- (115) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.
- (116) Wasielewski, M.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 11080.
- (117) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3974.
- (118) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 7242.
- (119) DeCosta, D. P.; Pincok, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8948.
- (120) Closs, G. L.; Calcaterra, L. T.; Green, L. T.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673–3683.
- (121) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Green, N. S. *J. Phys. Chem.* **1989**, *93*, 1173–1176.
- (122) Closs, G. L.; Liang, N.; Miller, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 8740–8741.
- (123) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1990**, *112*, 5353–5354.
- (124) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652–2653.
- (125) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751–3753.
- (126) Closs, G. L. In *Photochemical Energy Conversion*; Norris, J. R., Meisel, D., Eds.; Elsevier: Amsterdam, 1989; pp 23–31.