Acc. Chem. Res. **1989**, *22*, 15–21

Carbenic Reactivity Revisited

ROBERT A. MOSS

Wright and Rieman Laboratories, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

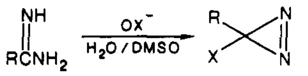
Received August 1, 1988 (Revised Manuscript Received October 3, 1988)

In 1980, we published an Account of "Carbenic Selectivity in Cyclopropanation Reactions".[1] There, we attempted to show how simple competitive kinetics experiments,[2] together with frontier molecular orbital (FMO) theory, could rationalize the selectivities expressed in this simplest of cycloaddition reactions, the (1 + 2) addition of a singlet carbene (CXY) to an alkene.[3] The study of carbene/alkene additions has since increased in importance. The reactants are small enough to be the subject of high quality ab initio calculations, so that (at least portions of) reasonably accurate energy surfaces can be generated for these cycloadditions. Moreover, current spectroscopic and fast kinetic methods make it possible to derive experimental data for comparison with the theoretical results. Together, these two approaches promise to yield instructive paradigms for chemical reactivity theory. One especially interesting aspect is that these cycloadditions span the kinetic range from near diffusion control ($\geq 10^9$ M^{-1} s^{-1}) to $\leq 10^3$ M^{-1} s^{-1}, so that it should be possible to determine how structural factors influence the behavior of reactants that traverse very low, moderate, or appreciable energy barriers.

Our earlier efforts focused on "classical" experimental methods. Indeed, an empirical correlation based on linear free energy relations did help characterize ambiphilic[4] as well as nucleophilic and electrophilic carbenes, while FMO theory and ab initio calculations[5] provided an appropriate theoretical counterpoint.

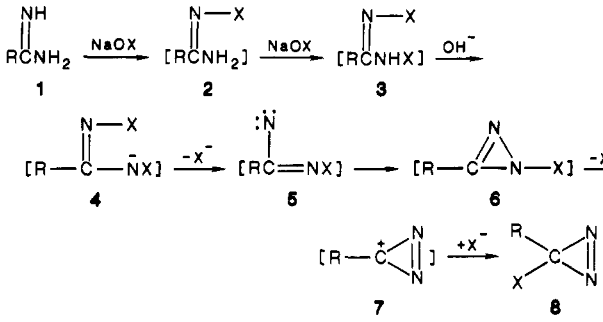
However, we warned that although we possessed a "workable, predictive, semiquantitative theory and a parallel body of congruent experimental results", we should be prepared for modifications upon the advent of new computational or experimental data, particularly absolute rate constants for CXY/alkene additions.[1] In fact, those developments have transformed the landscape of carbenic reactivity during the past eight years; the diazirine exchange reaction[6] afforded many new precursors for heretofore difficultly accessible ambiphilic and nucleophilic carbenes; nanosecond laser flash photolysis[7] provided absolute rate constants and activation parameters for numerous carbene/alkene cycloadditions; and the continuing application of theory helped us revise and refine our view of these reactions. In this Account we will try to integrate the new results into a coherent overview.

Diazirine Exchange. In order to study the chemistry of singlet carbenes at a fundamental level, we must have a menagerie of structurally diverse, spectroscopy-compatible precursors. The diazirines, because of their innocuous nitrogen leaving group, moderate stability, and tolerance of heteroatomic substituents, have assumed central importance. The Graham hypohalite oxidation of amidines to 3-halodiazirines, eq 1, was the initial breakthrough.[8] In this one-pot reaction, X can be Cl or Br, and R (determined by the availability of the amidine) can be alkyl, cycloalkyl, haloalkyl, aryl, vinyl, alkoxy, or aryloxy.



(1)

There is reason to believe that Graham's original mechanism, eq 2, is largely correct.[9] Its key features include successive N-halogenations of the amidine to *N*-halo (2) and *N,N'*-dihalo amidines (3); base-catalyzed conversion of 3 to the *N*-haloisodiazirine (6), either directly (4 → 6) or via α-elimination/closure involving the imino nitrene (5); ionization of 6 to diazirinium ion 7; and collapse of 7 with halide ion to give halodiazirine 8. The permissive intermediacy of 2 and 3 was demonstrated (for R = *i*-Pr and OMe) by independent synthesis and base-catalyzed conversion to 8.[9] The participation of 4–7 remains more or less conjectural, but isodiazirine 6 does appear to be a reasonable precursor of 8. Experimental analogy exists in the isoelectronic isomerizations of *C*-haloazirines,[10] and ab initio calculations indicate that 6 → 8 should be exothermic by ~18 kcal/mol when R = Me.[11]



(2)

The most important feature of Graham's mechanism is its suggestion that diazirinium ion 7 is an interme-

Robert A. Moss received his doctoral and postdoctoral training at the University of Chicago (Prof. G. L. Closs) and at Columbia University (Prof. R. Breslow). He is Professor of Chemistry at Rutgers University, where he has been a faculty member since 1964. He has also been a Visiting Scientist or Professor at M.I.T., Oxford, The Weizmann Institute, the Politechnika (Warsaw), and the Hebrew University of Jerusalem.

---

(1) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

(2) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 5430. Doering, W. v. E.; Henderson, W. A., Jr. *Ibid.* **1958**, *80*, 5274.

(3) Doering, W. v. E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, *76*, 6162.

(4) Moss, R. A.; Fedorynski, M.; Shieh, W.-C. *J. Am. Chem. Soc.* **1979**, *101*, 4736.

(5) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

(6) Moss, R. A. In *Chemistry of Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. I, pp 99f.

(7) Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* **1984**, *225*, 1439.

(8) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(9) Moss, R. A.; Włostowska, J.; Guo, W.; Fedorynski, M.; Springer, J. P.; Hirshfield, J. M. *J. Org. Chem.* **1981**, *46*, 5048.

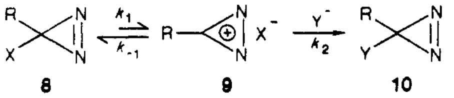
(10) Ciabattoni, J.; Cabell, M., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 1482.

(11) Krogh-Jespersen, K.; Young, C. M.; Moss, R. A.; Włostowski, M. *Tetrahedron Lett.* **1982**, *23*, 2339.

0001-4842/89/0122-0015$01.50/0

diate between **6** and **8**, for, as Graham implied, trapping of **7** by nucleophiles *other* than halide would make many new diazirines available. [Indeed, Graham did find some **8** (R = Me, X = OAc) when reaction 1 was carried out in the presence of acetate.[8]] Although ab initio calculations indicate thermodynamic instability and antiaromaticity for the parent diazirinium ion,[12] diazirinium halide *ion pairs* are reasonable species to be generated from **6** in polar solvents;[9,11] we estimate ~23 kcal/mol as the energy required for ionization of **6** (R = Me, X = Cl).[11]

Considerations such as these suggested the possibility of a *diazirine exchange reaction*, where initial 3-halodiazirine ionization to an ion pair (**8** → **9**) would be followed by capture of the diazirinium ion by an external nucleophile, Y^-, affording the new diazirine, **10**; eq 3. We were initially skeptical because of our estimate that **9** lay 18 + 23 ~ 41 kcal/mol above **8**, but our doubts were belayed, if not dispelled, by the first successful demonstration of diazirine exchange. Thus, the reaction of sodium methoxide in dimethylacetamide with 3-bromo-3-phenyldiazirine[8] in dimethylacetamide–HMPA (−10 °C/1 h) gave the rather unstable **10** (R = Ph, Y = OMe).[13]



(3)

8 **9** **10**

Analogous exchanges could be carried out with fluoride, by using molten, nearly anhydrous $n\text{-}Bu_4N^+F^-$ both as a source of the powerfully nucleophilic F^- and as a highly polar solvent to support ionic reactions.[14,15] Thus, **8** (R = Ph, X = Cl or Br) could readily be converted to **10** (R = Ph, Y = F), the first fluorodiazirine prepared without the use of elemental fluorine in the reaction sequence.[14] The reaction was extended to the preparation of various arylfluorodiazirines in ~70% yield using **8** (R = Ar, X = Br) as starting materials.[16]

Moreover, the availability of 3-phenoxy-3-chlorodiazirine[17] and 3-methoxy-3-chloro(or bromo)diazirine[8] by Graham oxidation implied that diazirine precursors for fluoroalkoxy-, fluoro(aryloxy)-, alkoxy(aryloxy)-, and dialkoxycarbenes would be available by methoxide or fluoride exchange. Indeed, **8** (R = PhO, X = Cl) affords **10** (R = PhO, Y = F) with molten $n\text{-}Bu_4N^+F^-$,[14,18] and a similar reaction with methoxybromodiazirine gives **10** (R = MeO, Y = F).[19] Furthermore, low-temperature exchange with NaOMe/DMF converts **8** (R = PhO or MeO, X = Cl) to the dioxydiazirines **10** (R = PhO or MeO, Y = MeO).[20,21] Although the 3,3-dioxydiazirines are rather unstable ($\tau_{1/2}$ in pentane ~20–60 min at 25 °C), these precursors do permit the study of the nucleophilic dioxycarbenes PhOCOMe and $(MeO)_2C$.

ELECTROPHILES	AMBIPHILES	NUCLEOPHILES
[MeCX][8]	[MeOCX][8]	MeOCOPh[20]
[PhCX][8]	[PhOCX][17]	MeOCOMe[21]
MeCF[25]	MeOCF[19]	$PhCNMe_2$[23]
PhCF[14,16]	PhOCF[14,18]	
MeCCN[25]	PhCOMe[13,27]	
PhCCN[14,22]	MeCOMe[25]	

Figure 1. Carbenes available from diazirines prepared by the two-step sequence of eq 4. The carbenes are roughly classified by "philicity". Carbenes in brackets are obtainable from diazirines directly produced by the Graham oxidation of amidines,[8] eq 1, X = Cl or Br. Superscripts indicate references.

Not only fluoride and methoxide but also cyanide,[14,22] amines,[23] and azide ion[14,16] can function as nucleophiles in diazirine exchange reactions. Cyano- and aminodiazirines can be prepared as precursors to cyano- and aminocarbenes, but we could not isolate the aminodiazirines that appear to decompose under the conditions of their formation.[23] This is also true of azidodiazirines [e.g., **10** (R = Ar, Y = N_3)], which lose 2 mol of nitrogen, affording nitriles in high yields.[14,16] Theoretical analysis suggests that this unusual fragmentation reaction is "concerted" and eschews stepwise loss of N_2 through such intermediates as nitrenodiazirines or azidocarbenes.[16]

If the diazirinium ion mechanism, eq 3, correctly accounts for the exchange reactions of phenylbromodiazirines via phenyldiazirinium ion (**9**, R = Ph), then *methyl*diazirinium ion (**9**, R = Me) might be an accessible intermediate from methylbromodiazirine (**8**, R = Me, X = Br); for, in the isoelectronic cyclopropenium ion series, trimethyl substitution is more stabilizing than triphenyl substitution.[24] Methylbromodiazirine[8] does indeed readily exchange with F^-, MeO^-, and CN^- to give the new diazirines **10** (R = Me; Y = F, OMe, and CN), which are precursors of fluoro-, methoxy-, and cyanomethylcarbenes.[25]

The diazirinium ion mechanism of eq 3 is consistent with the chemistry just outlined and is supported by several observations.[16] However, we do not consider the mechanism of eq 3 to be definitively established. Dailey correctly points out that the fluoride exchange of **8** (R = CF_3, X = Br) to **10** (R = CF_3, Y = F) is unlikely to transit **9** with R = CF_3.[26] Perhaps an addition/elimination mechanism, initiated by nucleophilic addition to N=N, supercedes the ionization mechanism when **9** is too destabilized. Nevertheless, the *transformation* described by eq 3 works, and works rather generally. The two-step sequence of Graham oxidation, followed by diazirine exchange, eq 4, thus makes available a wide variety of diazirine precursors for the generation of carbenes, including key exemplars of ambiphilic and

---

(12) Krogh-Jespersen, K. *Tetrahedron Lett.* **1980**, *21*, 4553.

(13) Włostowska, J.; Moss, R. A.; Guo, W.; Chang, M. J. *Chem. Commun.* **1982**, 432.

(14) Cox, D. P.; Moss, R. A.; Terpinski, J. *J. Am. Chem. Soc.* **1983**, *105*, 6513.

(15) Cox, D. P.; Terpinski, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3216.

(16) Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

(17) Moss, R. A.; Perez, L. A.; Włostowska, J.; Guo, W.; Krogh-Jespersen, K. *J. Org. Chem.* **1982**, *47*, 4177.

(18) Moss, R. A.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Org. Chem.* **1986**, *51*, 2168.

(19) Moss, R. A.; Fedorynski, M.; Terpinski, J.; Denney, D. Z. *Tetrahedron Lett.* **1986**, *27*, 419.

(20) Moss, R. A.; Włostowski, M.; Terpinski, J.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 3811.

(21) Moss, R. A.; Włostowski, M.; Shen, S.; Krogh-Jespersen, K.; Matro, A. *J. Am. Chem. Soc.* **1988**, *110*, 4443.

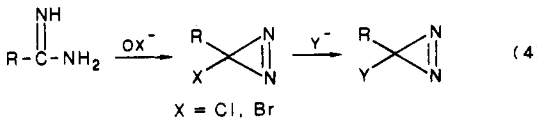
(22) Moss, R. A.; Kmiecik-Lawrynowicz, G.; Cox, D. P. *Synth. Commun.* **1984**, *14*, 21.

(23) Moss, R. A.; Cox, D. P.; Tomioka, H. *Tetrahedron Lett.* **1984**, *25*, 1023.

(24) Ciabattoni, J.; Nathan, E. C., III *Tetrahedron Lett.* **1969**, 4997. Breslow, R.; Höver, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168. Kerber, R. C.; Hsu, C.-M. *Ibid.* **1973**, *95*, 3229.

(25) Moss, R. A.; Fedorynski, M.; Kmiecik-Lawrynowicz, G.; Terpinski, J. *Tetrahedron Lett.* **1986**, *27*, 2707.

(26) Dailey, W. P. *Tetrahedron Lett.* **1987**, *28*, 5801.



(4)

nucleophilic carbenic reactivity such as FCOMe and $(MeO)_2C$. Figure 1 indicates the spectrum of carbenes available from diazirines via sequence 4.

These diazirines are ideal precursors for UV and IR spectroscopic studies of carbenes, opening the way for matrix isolation structural studies, as well as transient kinetic studies in solution. The latter provide absolute rates, activation parameters, and energy surface exploration for the classical reactions of carbenes. Simple carbenes are small molecules, easily handled by modern computational methods, so that we anticipate enormously fruitful interplay here between theory, spectroscopy, and reaction chemistry.

Carbenic Philicity. After Doering described methylene as "the most indiscriminate reagent known in organic chemistry",[28] making sense and order out of carbenic reactivity became one of my enduring tasks.[29] It became clear quite early that substituted carbenes were less reactive and more discriminating than methylene and that carbene/alkene addition reactions provided an expedient tool to measure carbenic selectivity or "philicity".[2,3,30,31] In order to systematize the growing body of data, we introduced the concept of a "carbene selectivity index", m_{CXY}.[1,32,33a] This was defined and measurable (for "electrophilic" carbenes) as the least-squares slope of the correlation between $\log (k_i/k_0)_{CXY}$ vs $\log (k_i/k_0)_{CCl_2}$, where the relative reactivities referred carbene additions to a "standard set" of (electron-rich or "nucleophilic") alkenes. The observed dependence of m_{CXY} on the X and Y substituents of nine carbenes, CXY, was well correlated by eq 5, where $\sum_{X,Y}$ represented the sums of the appropriate substituent constants for X and Y, m_{CCl_2} was set equal to unity, and the coefficients were determined by multiple least-squares fitting of the data.

$$m_{CXY} = -1.10\textstyle\sum_{X,Y}\sigma_R^+ + 0.53\textstyle\sum_{X,Y}\sigma_I - 0.31 \qquad (5)$$

Using measured or calculated values of m_{CXY} from eq 5, we constructed a carbene selectivity spectrum, locating both known and uninvestigated carbenes according to the magnitude of m_{CXY}.[1] Not only did eq 5 afford an evaluation of carbenic discrimination in olefin cycloaddition reactions, but it nicely paralleled the operational distinction between such *electrophilic* carbenes as CCl_2 and CF_2, which added with increasing rate to olefins of increasing π-electron richness, and *nucleophilic* carbenes, such as $(MeO)_2C$, which added with increasing rate to olefins of decreasing π-electron availability.

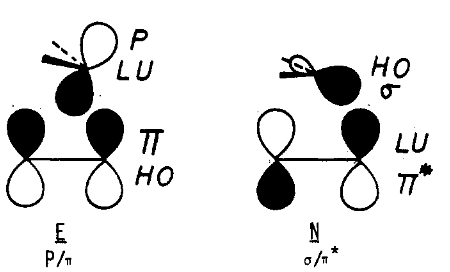


Figure 2. HOMO–LUMO interactions in carbene/alkene cycloadditions.

Most importantly, eq 5 focused attention on the probable existence of "in-between" or *ambiphilic* carbenes, which should exhibit a parabolic dependence on alkene π-electron character, with high reactivity toward both electron-rich and electron-poor alkenes, but low reactivity toward alkenes of intermediate character. Indeed, because the electrophilic carbenes known in 1977 had $m_{CXY} < 1.50$, whereas the known nucleophilic carbenes had $m_{CXY} > 2.2$, we decided that MeOCCl ($m_{CXY}^{calcd} = 1.59$) was a good candidate ambiphile. Experiments (Table I) proved this to be the case.[4] Equation 5 and standard tables of substituent constants soon directed us to other ambiphiles; their relative reactivities toward selected olefins are summarized in Table I, together with the m_{CXY} values calculated from eq 5.

Across the range of π and π^* orbitals defined by this set of olefins, carbenes such as MeCCl and CCl_2 are clearly electrophiles, whereas MeOCCl demonstrates the parabolic selectivity pattern anticipated for an ambiphile.[1,4] PhOCCl[17] and PhOCF[18] also are ambiphiles, although steric retardation apparently inhibits their additions to the hindered alkene tetramethylethylene.

Limitations of the pure empirical approach begin to appear, however, when we examine the behavior of PhCCl, PhCF, MeOCPh, and MeOCMe. PhCCl and PhCF react slightly more rapidly with acrylonitrile than with methyl acrylate.[34a] Is this due to a borderline ambiphilicity? Yes, and use of the even more electron poor substrate α-chloroacrylonitrile brings out this "latent" ambiphilicity.[38] Therefore PhCCl and PhCF, despite their low m_{CXY} values, can be classified as ambiphiles. Even more strikingly, MeOCPh[27] and MeOCMe,[37] with $m_{CXY} < 1.5$, show pronounced nucleophilic properties. Indeed, on the scale of Table I, their relative reactivities toward α-chloroacrylonitrile are ~16 000 (MeOCPh)[38] and 22 300 (MeOCMe).[37]

The deficiencies of the empirical approach probably stem from the "calibration" of eq 5 with carbenes that are primarily electrophilic and alkenes that are primarily electron rich.[32] An equation so thoroughly grounded in the "electrophilic" sector of the carbene selectivity

---

(27) Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Lawrynowicz, G.; Włostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341.

(28) Doering, W. v. E.; Buttery, R. G.; Laughlin, R. G.; Chaudhuri, N. *J. Am. Chem. Soc.* **1956**, *78*, 3224.

(29) Moss, R. A.; Jones, M., Jr. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, pp 45f.; *Ibid.* 1981; Vol. 2, pp 59f.; *Ibid.* 1978; Vol. 1, pp 69f. Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1975; Vol. II. Jones, M., Jr., Moss, R. A., Eds. *Carbenes*; Wiley: New York, 1973; Vol. I. Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964.

(30) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131.

(31) Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I, pp 153f.

(32) Moss, R. A.; Mallon, C. B.; Ho, C.-T. *J. Am. Chem. Soc.* **1977**, *99*, 4105.

(33) (a) Moss, R. A.; Mamantov, A. *J. Am. Chem. Soc.* **1970**, *92*, 6951. (b) Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1979**, 4721.

(34) (a) Moss, R. A.; Lawrynowicz, W.; Hadel, L. M.; Hacker, N. P.; Turro, N. J.; Gould, I. R.; Cha, Y. *Tetrahedron Lett.*. **1986**, *27*, 4125. (b) Moss, R. A.; Whittle, J. R.; Freidenreich, P. *J. Org. Chem.* **1969**, *34*, 2220.

(35) Moss, R. A.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3828.

(36) Moss, R. A.; Włostowska, J. *Tetrahedron Lett.* **1988**, *29*, 2559.

(37) Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Włostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563.

(38) Moss, R. A.; Fan, H.; Hadel, L. M.; Shen, S.; Włostowska, J.; Włostowski, M.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1987**, *28*, 4779. On the scale of Table I, k_{rel} values toward $CH_2{=}CClCN$ are 8.3 (PhCCl) and 10.2 (PhCF).

Table I
Relative Reactivities of Carbenes toward Alkenes[a]

alkene	MeCCl[b]	CCl_2[c]	PhCCl[d]	PhCF[e]	MeOCCl[f]	PhOCCl[g]	PhOCF[h]	MeOCPh[i]	MeOCMe[j]
$Me_2C{=}CMe_2$	7.44	78.4	25.5	33.2	12.6	3.0	7.14	0.32	
$Me_2C{=}CHMe$	4.69		16.0	12.0			17.9	3.4	2.13
$Me_2C{=}CH_2$	1.92	4.89	5.0	6.67	5.43	7.3	14.3	10.6	2.18
trans-MeCH=CHMe	1.00	1.00	1.00	1.00	1.00	1.00		1.00	1.00
$n\text{-}C_4H_9CH{=}CH_2$						0.36	1.00	0.74	
$CH_2{=}CHCO_2Me$	0.078	0.060	0.50	0.74	29.7	3.7	18.7	172	362
$CH_2{=}CHCN$	0.074	0.047	0.55	0.80	54.6	5.5	33.6	445	686
m_{CXY}[k]	0.58	0.97	0.71	0.96	1.59	1.49	1.74	1.34	1.21

[a] Data are at 25 °C except for CCl_2 (80 °C) and PhOCF (50 °C). All carbenes were generated from diazirines except CCl_2, which was produced by the thermolysis of $PhHgCCl_2Br$. [b] References 33a,b. [c] Reference 33b. [d] References 34a,b. [e] References 34a, 35. [f] Reference 4. [g] Reference 17. [h] Reference 18. [i] References 27, 36. [j] Reference 37. [k] Calculated from eq 5.

Table II
Differential Orbital Energies (eV) for Carbene/Alkene Additions[a]

	CCl_2		MeOCCl		MeOCMe	
alkene	$\Delta\epsilon_E$	$\Delta\epsilon_N$	$\Delta\epsilon_E$	$\Delta\epsilon_N$	$\Delta\epsilon_E$	$\Delta\epsilon_N$
$Me_2C{=}CMe_2$	8.58	13.71	10.73	13.09	12.31	11.68
$Me_2C{=}CHMe$	8.99	13.68	11.14	13.06	12.72	11.65
$Me_2C{=}CH_2$	9.55	13.63	11.70	13.01	13.28	11.60
trans-MeCH=CHMe	9.43	13.54	11.58	12.92	13.16	11.51
$CH_2{=}CHCO_2Me$	11.03	12.24	13.18	11.62	14.76	10.21
$CH_2{=}CHCN$	11.23	11.65	13.38	11.03	14.96	9.62

[a] See eq 6a,b. Orbital energies can be found in ref 1 and 5. For MeOCMe (*trans*-carbene conformer), LU = 4.04 eV, HO = −9.41 eV.[37]

spectrum may be very helpful in guiding the search for ambiphiles,[4] but cannot be expected to quantitatively correlate their selectivities, as well as those of nucleophilic carbenes.

Rather than attempting to repair eq 5 by the inclusion of additional parameters and coefficients, it now seems preferable to use FMO theory in the primary rationalization of carbenic philicity.[1,4,5,39] In the (1 + 2) cycloaddition of any singlet carbene to an alkene, the carbene is inherently *both* an electrophile and a nucleophile. What determines the carbene's expressed philicity is whether, in the transition state, it is the $[\text{LUMO}_{\text{carbene}}\text{–HOMO}_{\text{alkene}}]$ (p/π) electrophilic (E) orbital interaction or the $[\text{HOMO}_{\text{carbene}}\text{–LUMO}_{\text{alkene}}]$ (σ/π^*) nucleophilic (N) interaction that is dominant; see Figure 2. If both interactions are comparably important, the carbene will exhibit ambiphilic selectivity.[40]

The FMO approach can be applied in a semiquantitative fashion to the rationalization of carbenic philicity[1,4,5] and continues to serve well in analyses of the more recently studied ambiphiles (Table I). Although the "dominant" orbital interaction in a carbene/alkene cycloaddition transition state will be determined by both the differential orbital energies and extent of overlap of the two HOMO/LUMO combinations, consideration of the energy terms alone usually suffices to rationalize or predict philicity. For the carbenes, ab initio calculations have made LUMO (p) and HOMO (σ) energies readily available,[5,41] whereas olefinic LUMO (π^*) and HOMO (π) energies are available from spectroscopy.[42]

It is probably sinful to "mix" calculated, uncalibrated carbene orbital energies with experimental values for alkenes, but the results of this procedure do seem to mirror reality. According to FMO theory,[39] the *stabilization* of a cycloaddition transition state (TS) depends *inversely* on the differential energies of the interacting "frontier" molecular orbitals; i.e., neglecting overlap, a smaller $\Delta\epsilon$ results in a greater TS stabilization, a lower activation energy, and a faster cycloaddition. To estimate the FMO interactions of Figure 2, we insert orbital energies into eq 6a and 6b, where $\Delta\epsilon_E$ and $\Delta\epsilon_N$ represent the differential orbital energies corresponding to the electrophilic and nucleophilic interactions. Results for CCl_2, MeOCCl, and MeOCMe appear in Table II.

$$\Delta\epsilon_E = \epsilon^{LU}_{CXY} - \epsilon^{HO}_{C=C} = p - \pi \tag{6a}$$

$$\Delta\epsilon_N = \epsilon^{LU}_{C=C} - \epsilon^{HO}_{CXY} = \pi^* - \sigma \tag{6b}$$

The implications of Table II are clear: over the given set of alkenes, CCl_2 should be primarily electrophilic (dominated by a smaller $\Delta\epsilon_E$ term) and MeOCMe should be primarily nucleophilic (dominated by $\Delta\epsilon_N$), but MeOCCl should be ambiphilic. That is, its reactions will be governed by $\Delta\epsilon_E$ when the alkenes are electron rich (high-lying π orbitals), but dominated by $\Delta\epsilon_N$ when the alkenes bear electron-withdrawing groups that lower both π^* and π orbital energies. A crossover or "mechanism change" from predominantly electrophilic to nucleophilic addition results as we proceed from $Me_2C{=}CMe_2$ to $CH_2{=}CHCN$ substrates and is reflected in a parabolic or ambiphilic selectivity pattern. Table I displays these trends in the experimental results. The electrophilicity and ambiphilicity of CCl_2 and MeOCCl are clearly apparent, whereas the nucleophilicity of MeOCMe is strongly expressed, even if its electrophilicity is not totally suppressed.

---

(39) Apposite discussions include: Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. Sustmann, R. *Tetrahedron Lett.* **1971**, 2717, 2721. Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361. Mayor, C.; Wentrup, C. *J. Am. Chem. Soc.* **1975**, *97*, 7467. Jones, W. M.; LaBar, R. A.; Brinker, U. H.; Gebert, P. H. *J. Am. Chem. Soc.* **1977**, *99*, 6379, note 27. Schoeller, W. W.; Brinker, U. H. *Z. Naturforsch.* **1980**, *35b*, 475. Schoeller, W. W. *Tetrahedron Lett.* **1980**, *21*, 1505, 1509. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

(40) This is nicely illustrated by the "broken" Hammett plots characteristic of the additions of ambiphiles (MeOCCl, PhOCCl) to styrenes: Moss, R. A.; Guo, W.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1982**, 23, 15. Moss, R. A.; Perez, L. *Ibid.* **1983**, *24*, 2719.

(41) See also ref 4, 17, 18, and 27.

(42) See ref 1, Table IV for values and references.

Table III
Carbenic Philicity of Selected Carbenes

carbene	ϵ_{HO},[a] eV	ϵ_{LU},[a] eV	exptl philicity[b]
CF$_2$	-13.38	1.89	E
CCl$_2$	-11.44	0.31	E
MeOCCl	-10.82	2.46	A
PhOCF	-11.81	2.56	A
MeOCMe	-9.41	4.04	N
MeOCOMe	-10.62	4.34	N

[a] The oxycarbenes are considered only in their trans configurations. The orbital energies are calculated at the 4-31G level after geometry optimization at the STO-3G level; see ref 5, 18, 21, and 37. [b] Predominant experimental philicities; E = electrophilic, A = ambiphilic, N = nucleophilic.

We can generalize that carbenic electrophilicity is favored by a low-lying HOMO or σ orbital (making electron donation unfavorable) and an accessible, low-lying LUMO or p acceptor orbital. Conversely, carbenic nucleophilicity requires a high-lying HOMO for ready electron donation and a high-lying inaccessible LUMO. As long as the set of substrates is held constant (as in Table I), inspection of the ab initio carbene frontier orbital energies (Table III) gives us an immediate sense of the anticipated philicities. Thus, CF$_2$ is an electrophile almost by default; its extremely low lying σ orbital contains electrons that are unavailable for donation. The electrophilicity of CCl$_2$, on the other hand, surely reflects its low-lying p or LUMO, which is readily accessible to alkene π donors. MeOCCl and PhOCF feature σ and p orbitals that lie at "intermediate" energies; depending on the π and π^* levels of their substrates, either $\Delta\epsilon_E$ or $\Delta\epsilon_N$ will dominate their cycloadditions with an attendant ambiphilic reactivity pattern. Finally, the high-lying, relatively inaccessible LUMOs of MeOCMe and (MeO)$_2$C, together with their relatively high donor HOMOs, insure their strongly nucleophilic behavior.[43]

Absolute Rate Constants. A fundamental examination of structure–reactivity relationships in this simplest of cycloadditions requires absolute rate constants, k_{abs}, that provide activation parameters, permitting us to probe the origins of selectivity in reactions that traverse relatively "flat" energy surfaces. The appropriate kinetic regime turns out to be $\sim 10^4$–10^9 M^{-1} s^{-1}, which requires nanosecond laser flash photolytic spectroscopy to visualize the transient carbenes in solution. Our laboratory, together with that of N. J. Turro at Columbia University, found that the arylhalocarbenes were well-suited to this technique, and began to collect the appropriate data in 1980.[44]

The apparatus, output, and methodology have been described in some detail[45] and will not be discussed here. We found that the second-order rate constants for the additions of ArCX to simple alkenes were sensitive to structural variations in both the carbene and the alkene, in accord with previous conclusions drawn from relative reactivity studies;[1,31] cf. Table IV.[46] Thus, k_{abs} ranged from near diffusion controlled (BrCPh + Me$_2$C=CMe$_2$) over a span of $\sim$400-fold (FCPh + BuCH=CH$_2$). With each alkene, the rate constants or *reactivities* were in the order BrCPh > ClCPh > FCPh, the inverse of the anticipated carbene stability order based on halogen lone pair interactions with the carbenic 2p orbitals.[1,5,31] Moreover, as measured by the ratio of the largest to smallest rate constants ("spread"), the *selectivities* of the carbenes followed the order FCPh > ClCPh > BrCPh, indicative of a reactivity/selectivity correlation of the "normal" or inverse type.[46]

Table IV
Absolute Rate Constants for Additions of XCPh to Alkenes[a]

alkene	FCPh	ClCPh	BrCPh
Me$_2$C=CMe$_2$	1.6×10^8	2.8×10^8	3.8×10^8
Me$_2$C=CHMe	5.3×10^7	1.3×10^8	1.8×10^8
trans-MeCH=CHEt	2.4×10^6	5.5×10^6	1.2×10^7
n-BuCH=CH$_2$	0.93×10^6	2.2×10^6	4.0×10^6
"spread"[b]	172	127	95

[a] Rate constants are in L/(mol s) and were determined in alkene/isooctane solution at 23 °C by laser flash photolysis. Reproducibilities are <±10%. [b] Rate constant ratio for additions to Me$_2$C=CMe$_2$ vs *n*-BuCH=CH$_2$.

With the ability to measure k_{abs}, it becomes possible to determine activation parameters for these carbene/alkene cycloadditions.[47,48] For example, measurements of k_{abs} as a function of *pressure* afford volumes of activation ($\Delta V^{\ddagger}$) for the additions of PhCX to tetramethylethylene and *trans*-2-pentene.[47] In hydrocarbon solvents, $\Delta V^{\ddagger}$ ranges from -18 ± 2 cm^3/mol (FCPh + *trans*-pentene) to -10 ± 1 cm^3/mol (BrCPh + Me$_2$C=CMe$_2$); $\Delta V^{\ddagger}$ values for ClCPh additions are $\sim 14 \pm 3$ cm^3/mol.

The negative $\Delta V^{\ddagger}$ values indicate that transition-state volumes are smaller than the initial combined reactant volumes, so that pressure accelerates these reactions. We see a mild trend toward a more negative $\Delta V^{\ddagger}$ with increasing carbenic stability, but there is significant imprecision in the data. A negative $\Delta V^{\ddagger}$ is commonly observed in cycloaddition reactions, where two molecules condense to form a single product molecule.[49] However, the magnitudes of $\Delta V^{\ddagger}$ for our carbene additions are small by comparison; e.g., $\Delta V^{\ddagger}$ for Diels–Alder reactions often reaches ~ -40 cm^3/mol. The smaller volumes of activation for the carbene reactions are consistent with *early*, loose transition states, where bond formation is not far advanced. This, in turn, implies the very low activation energies that are, in fact, observed.[45,48]

The dependence of k_{abs} on temperature has been intensively examined for the additions of arylhalocarbenes to alkenes. Our initial study[48] involved PhCCl and the alkenes of Table IV. Arrhenius correlations afforded $E_a \sim 1$ kcal/mol for the additions to *trans*-pentene and 1-hexene. Most surprising was the observation of *negative* activation energies (~ -1 to -2 kcal/mol) for the reactions of PhCCl with trimethyl- and tetramethylethylene. Preexponential (A) values ranged from 2×10^7 to 6×10^7 M^{-1} s^{-1}.

How does one interpret a negative E_a, i.e., an increase in rate constant with a decrease in temperature? Two approaches have been suggested. The first postulates the incursion of a reversibly formed carbene/alkene

---

(43) The calculated geometries of these oxycarbenes are discussed in ref 21 and 37.

(44) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576.

(45) Gould, I. R.; Turro, N. J.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.

(46) Cox, D. P.; Gould, I. R.; Hackey, N. P.; Moss, R. A.; Turro, N. J. *Tetrahedron Lett.* **1983**, *24*, 5313.

(47) Turro, N. J.; Okamoto, M.; Gould, I. R.; Moss, R. A.; Lawrynowicz, W.; Hadel, L. M. *J. Am. Chem. Soc.* **1987**, *109*, 4973.

(48) Turro, N. J.; Lehr, G. F.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754.

(49) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407.

Table V
Differential Activation Parameters for PhCCl Additions[a]

alkene	$\Delta\Delta H^\ddagger$, kcal/mol	$\Delta\Delta S^\ddagger$, eu	$\Delta\Delta G^\ddagger$, kcal/mol
$Me_2C{=}CMe_2$	−4.4	−23	2.2
$Me_2C{=}CHMe$	−3.7	−22	2.7
trans-MeCH=CHEt	−1.6	−20	4.3
1-hexene	−1.5	−21	4.5

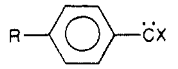
[a] Data from ref 48. The estimated errors in $\Delta\Delta G^\ddagger$ are ±0.5 kcal/mol.

complex that either dissociates back to reactants or proceeds to the product cyclopropane.[45,48] Mathematical treatment of the experimental data according to this scheme affords *differential* activation parameters for dissociation of the complex vs completion of the cyclopropanation; cf. Table V.[48] What is most interesting here is the obvious importance of entropy. Note, however, that the values of $\Delta\Delta S^\ddagger$ in Table V are effectively equal for each substrate, so that the order of the rate constants depends on the relative differential enthalpies of activation for cyclopropanation vs dissociation of the carbene/alkene complex. A de facto enthalpic control operates, where the differences in $\Delta\Delta G^\ddagger$ reflect differences in $\Delta\Delta H^\ddagger$, leading to the classical olefin reactivity sequence.[30]

There are precedents in reactive-intermediate chemistry for the postulation of a complex to rationalize negative activation energies,[45] and transient complexes have become popular (notorious?) for the ease with which they can account for kinetic complexities in product-based analyses of competitive carbene reactions.[50] However, carbene/alkene complexes have never been observed, nor is their existence supported by reasonably high level calculations.[51,52] If they do exist, they are likely to be weakly bound proximity or contact pairs within solvent cages.[45,48]

The second proffered origin of the negative activation energies is due to Houk et al.,[51,53] who calculated ΔH as a function of reactant separation for the additions of CBr_2, CCl_2, and CF_2 to tetramethylethylene and isobutene. They also modeled ΔS for these reactions and derived values of ΔG. Their key conclusion was that, in the addition of a very reactive carbene (CBr_2) to a reactive alkene ($Me_2C{=}CMe_2$), ΔH decreased *continually* along the reaction coordinate (i.e., $\Delta H^\ddagger$ and E_a were negative), but that there was a free-energy barrier to addition ($\Delta G^\ddagger > 0$) because of a dominant unfavorable *entropy of activation*. The latter was largely due to the loss of translational, vibrational, and rotational entropy encountered as the two reactant molecules traversed the transition state required to form a single product molecule. With a more stable carbene (CF_2) there was a positive E_a and $\Delta H^\ddagger$ that added to the $\Delta G^\ddagger$ barrier, but entropy was still important.[51,53] The Houk model accounted naturally for the negative activation energies and simultaneously focused on the central role of entropy in carbenic additions, a point made earlier by Skell[30] and more recently by Giese.[54]

In order to examine the interplay of enthalpy, entropy, and structure in carbenic additions, we determined absolute rate constants and activation parameters for the additions of arylhalocarbenes **11a–e** to $Me_2C{=}CMe_2$ and 1-hexene. Carbenic reactivity decreased from **11a** to **11e**.[55] Rate constants ranged from $(1.7 \pm 0.05) \times 10^9$ M^{-1} s^{-1} for the fastest addition (**11a** + $Me_2C{=}CMe_2$) to $(5.0 \pm 0.3) \times 10^4$ M^{-1} s^{-1} for the slowest addition (**11e** + 1-hexene), affording a spread of 3400 in k_{abs}. Classical ideas about carbenic reactivity were manifested by the data; $Me_2C{=}CMe_2$ rate constants were ~100 times greater than those for 1-hexene with each carbene, and *p*-CF_3- or Br-substituted **11** were more reactive than *p*-CH_3O- or F-substituted **11**. Carbenic substituent effects were additive.



	R	X
11a	CF_3	Br
b	H	Br
c	H	Cl
d	H	F
e	CH_3O	F

Arrhenius activation energies were ~−1 to −2 kcal/mol for the additions to $Me_2C{=}CMe_2$ (except for **11e**, where $E_a \sim 0$), but became positive for the additions to 1-hexene. The largest E_a (**11e** + 1-hexene) was 3 kcal/mol.[55] The data was most conveniently analyzed in terms of the parameters shown in Table VI.

Here we observe that all of the reactions are entropy controlled; even in the "slow" **11e** + 1-hexene reaction, where $\Delta G^\ddagger = {\sim}11$ kcal/mol, $\Delta H^\ddagger$ contributes only 2.5 kcal/mol, whereas the $-T\Delta S^\ddagger$ term adds 8.6 kcal/mol, or 78% of the total free-energy barrier. As we move toward the less reactive carbene/alkene pairings, $\Delta H^\ddagger$ does increase, but $-T\Delta S^\ddagger$ also increases. The overall rise of 6 kcal/mol in $\Delta G^\ddagger$ (from the upper left to lower right of Table VI) is composed of ~4 kcal/mol in $\Delta H^\ddagger$ and ~2 kcal/mol in $-T\Delta S^\ddagger$. Although $\Delta H^\ddagger$ changes from negative to positive with the structural evolution of the reactants, it does not become dominant. The importance of entropy in the reactions of **11a–e** is clearly consistent with Houk's model for carbene/alkene cycloadditions.[51-53]

We are reminded here of Skell's application of the Hammond postulate to structure–reactivity relations in carbene/alkene addition reactions:[30] reactive carbenes and alkenes should transit early, loose, entropy-dominated transition states, whereas less reactive carbenes and alkenes would traverse later, tighter, enthalpy-controlled transition states. Clearly, the extent of structural variation available with arylhalocarbenes and alkylethylenes is insufficient to pass from the entropy- to enthalpy-controlled regime. Indeed, the most selective version of **11**, *p*-MeOPhCF, is comparable to CCl_2,[55] for which entropic control and $\Delta H^\ddagger < 0$ are anticipated.[30,51,53]

In order to observe enthalpic dominance, we probably require a carbene at least as stable and selective as CF_2.[30,51,53] Now that the even more highly stabilized

---

(50) See, for example: Liu, M. T. H.; Soundararajan, N.; Paike, N.; Subramanian, R. *J. Org. Chem.* **1987**, *52*, 4223.

(51) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

(52) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291.

(53) Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4293.

(54) Giese, B.; Neumann, C. *Tetrahedron Lett.* **1982**, *23*, 3357. Giese, B.; Lee, W.-B.; Neumann, C. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 310 and earlier references.

(55) Moss, R. A.; Lawrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028.

Table VI
Activation Parameters for ArCX/Alkene Additions[a]

	tetramethylethylene				1-hexene			
carbene	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$-T\Delta S^\ddagger$	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$-T\Delta S^\ddagger$	$\Delta G^\ddagger$
p-$CF_3C_6H_4CBr$	-1.6	-22	6.6	5.0	-0.19	-25	7.4	7.2
PhCBr	-2.1	-25	7.4	5.3	0.40	-26	7.7	8.1
PhCCl	-2.3	-28	8.3	6.0	0.51	-27	8.0	8.5
PhCF	-2.3	-28	8.3	6.0	0.71	-29	8.6	9.3
p-$CH_3OC_6H_4CF$	-0.4	-27	8.0	7.6	2.5	-29	8.6	11

[a] Data are from ref 55 and are calculated at 298 K. Units are kcal/mol for $\Delta H^\ddagger$, $\Delta G^\ddagger$, and $T\Delta S^\ddagger$ and cal/(deg mol) for $\Delta S^\ddagger$.

species MeOCF and $(MeO)_2C$ are available from spectroscopically compatible precursors,[19,21] it should be possible to further probe enthalpy/entropy partition in carbenic cycloadditions. Indeed, dimethoxycarbene is sufficiently chromophoric to permit the measurement of absolute rate constants for its reactions,[21] so that activation parameters should soon be forthcoming.

Conclusion. The combined impacts of new carbene precursors, nanosecond kinetic methods, and realistic computations have greatly altered our detailed view of carbenic reactivity, while simultaneously integrating the newly emerging picture with the broader perspective of cycloaddition reaction theory. The entropic dominance manifested in carbene/alkene additions of very low $\Delta G^\ddagger$ is probably a feature of cycloaddition reactions in general, but we can see how the counterpoint between $\Delta H^\ddagger$, $\Delta S^\ddagger$, and carbenic structure underlies the classical reactivity pattern deduced from older, product-based studies. The continued application of sophisticated spectroscopic and computational methods to carbenic additions should now point toward the detailed mapping of their reaction surfaces.

I am enormously indebted to my associates, whose names appear in the references. Special thanks go to my colleagues, Prof. K. Krogh-Jespersen (Rutgers) and Prof. N. J. Turro and Dr. I. R. Gould (Columbia), whose close collaborations over the past eight years were essential to the work described herein. I also note with deep appreciation the central and continuing role played by my associates from Poland. Finally, I thank the National Science Foundation for its support of our efforts.

Chemical Reactions and Energy Transfer Processes of Electronically Excited Group IIB Metal Atoms: Full Collisions and Half-Collisions

W. H. BRECKENRIDGE

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received April 19, 1988 (Revised Manuscript Received October 3, 1988)

I. Introduction

A major goal of modern dynamics is to characterize elementary chemical reactions or energy-transfer processes in a "state-to-state" fashion. One would like to prepare initial reagents in a known (and preferably variable) set of quantum states and then determine the different rates at which various possible sets of product quantum states are formed. Such measurements must be "single-collision" in nature, because collisional thermalization of the prepared reagents before the process of interest takes place, or of the nascent product states before detection, decreases the content of the dynamical information sought. Preparation, collision, and detection must therefore occur at very low pressures or within very short periods of time at moderate pressures.

We have concentrated on studies of collisional processes involving electronically excited group II metal atoms, using a laser pump–probe technique.[1-12,14-17,20-27]

Bill Breckenridge was born on October 14, 1941. His first experience with research in chemistry was as an undergraduate at Kansas University with Sherry Rowland. After a year of graduate research in physical chemistry at Leeds University with Fred Dainton and Don Baulch on a Fulbright fellowship in 1964, he completed his Ph.D. degree in physical and inorganic chemistry at Stanford University in 1968 under the direction of Henry Taube. Following postdoctoral research in physical chemistry with Tony Callear at Cambridge University and Terry Miller at Bell Labs, in 1971 he joined the faculty at the University of Utah, where he is now Professor of Chemistry.

(1) Breckenridge, W. H.; Umemoto, H. In *The Dynamics of the Excited State*; Lawley, K., Ed.; Advances in Chemical Physics; Wiley: New York, 1982; Vol. 50.

(2) Breckenridge, W. H. In *Reactions of Small Transient Species*; Clyne, M., Fontijn, A., Eds.; Academic Press: New York, 1983.

(3) Breckenridge, W. H.; Malmin, O. Kim; Nikolai, W. L.; Oba, D. *Chem. Phys. Lett.* **1978**, *59*, 38.

(4) Breckenridge, W. H.; Donovan, R. J.; Malmin, O. K. *Chem. Phys. Lett.* **1979**, *62*, 608.

(5) Breckenridge, W. H.; Oba, D. *Chem. Phys. Lett.* **1980**, *72*, 455.

(6) Breckenridge, W. H.; Malmin, O. K. *J. Chem. Phys.* **1981**, *74*, 3307.

(7) Breckenridge, W. H.; Umemoto, H. *J. Chem. Phys.* **1981**, *75*, 698.

(8) Breckenridge, W. H.; Malmin, O. K. *J. Chem. Phys.* **1982**, *76*, 1812.

(9) Breckenridge, W. H.; Umemoto, H. *J. Chem. Phys.* **1983**, *79*, 745.

(10) Breckenridge, W. H.; Umemoto, H. *Chem. Phys. Lett.* **1983**, *101*, 377.

(11) Breckenridge, W. H.; Umemoto, H. *J. Chem. Phys.* **1984**, *80*, 4168.

(12) Breckenridge, W. H.; Umemoto, H. *J. Chem. Phys.* **1984**, *81*, 3852.

(13) Kowalski, A.; Czajkowski, M.; Breckenridge, W. H. *Chem. Phys. Lett.* **1985**, *121*, 217.

0001-4842/89/0122-0021$01.50/0