16 J. Am. Chem. Soc. 1983, 105, 16-18

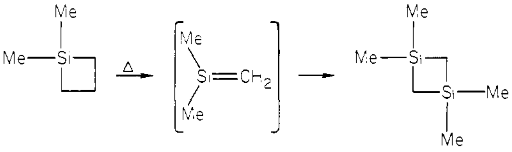
Relative Thermochemical Stabilities of 1-Methylsilaethylene and Dimethylsilylene by Ion Cyclotron Double Resonance Spectroscopy

C. F. Pau, W. J. Pietro, and W. J. Hehre*

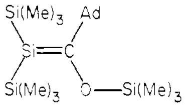
Contribution from the Department of Chemistry, University of California, Irvine, California 92717. *Received April 9, 1982*

Abstract: Heats of formation of 1-methylsilaethylene and dimethylsilylene of 18 and 46 kcal mol^{-1} have been obtained by using ion cyclotron double resonance spectroscopy. Their difference, 28 kcal mol^{-1} in favor of the silaolefin, contradicts the experimental findings of Dranak, Michl, and West and of Colin and Wood, both of which suggest thermal equilibrium favoring the silylene, and computational work on related systems of Schaefer, Köhler, and Lischka and of Pople which show the isomers to be of nearly equal stability.

Silicon analogues of olefins, e.g., **1**, have received considerable attention among chemists since they were first suggested as short-lived intermediates in the pyrolysis of silacyclobutanes.[1] Numerous chemical and physical-chemical experiments have been carried out on silaolefins during the past decade.[2] They have been generated and trapped under a variety of conditions.[3] An electron diffraction structure[4] and infrared[5] and photoelectron[6] spectra of gaseous **1** have been reported. Crystals of one stable compound, **2**, have been prepared and its structure has been obtained from X-ray techniques.[7]

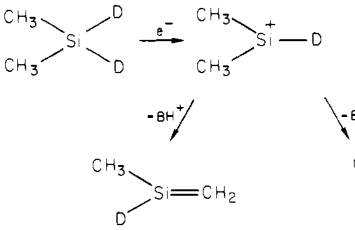


1



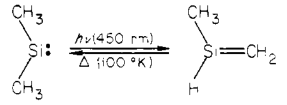
2

Scheme I



The thermochemistry of **1** has also been investigated experimentally. Early kinetic studied by Gusel'nikov and co-workers,[8] as reanalyzed by Walsh,[9] indicate a heat of formation of 7 ± 5 kcal mol^{-1}; this corresponds to a silicon–carbon π bond strength in the range of 34–44 kcal mol^{-1}, roughly half to two thirds of that noted for isobutene,[10] the hydrocarbon analogue. Recent work from our laboratory,[11] using ion cyclotron resonance spectroscopy, suggests values of 7 and 38 kcal mol^{-1} for the heat of formation and π bond energy in 1,1-dimethylsilaethylene. Theoretical molecular orbital calculations suggest a somewhat higher, 47 kcal mol^{-1}, π bond strength for **1**.[12] A similar value was previously obtained for parent silaethylene.[13,14]

Another silaolefin that has been extensively studied is the 1-methyl derivative, **3**, for which a heat of formation of 23 ± 5 kcal mol^{-1} has been inferred by Walsh on the basis of thermochemical data on the corresponding dimethyl compound, **1**.[9b] Drahnak, Michl, and West have observed the species in both argon and hydrocarbon matrices, formed upon irradiation at 450 nm of trapped dimethylsilylene, **4**.[15] They have also noted that slight



3 4

---

[1] N. S. Nametkin, V. M. Vdovin, L. E. Gusel'nikov and V. I. Zav'yalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 584 (1966).

[2] For a recent review see L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, **79**, 529 (1979).

[3] Examples include among many others: (a) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419, 1396 (1968); (b) L. E. Gusel'nikov, *J. Chem. Soc.*, **5**, 23 (1968); (c) N. S. Nametkin, L. E. Gusel'nikov, W. M. Vodvin, P. L. Grinberg, V. I. Zuv'yalov, and V. D. Oppengeim, *Dokl. Akad. Nauk SSSR*, **171**, 630 (1966); (d) R. D. Bush, C. M. Golino, G. D. Homer, and L. H. Sommer, *J. Organomet. Chem.*, **80**, 37 (1974); (e) R. D. Bush, C. M. Golino, D. N. Roark, and L. H. Sommer, *Ibid.*, **59**, C17 (1973); (f) N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, and V. M. Vodvin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1840 (1971); (g) N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, and V. M. Vodvin, *Dokl. Akad. Nauk SSSR*, **201**, 1365 (1971); (h) D. N. Roark and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 167 (1973); (i) C. M. Golino, R. D. Bush, D. N. Roark and L. H. Sommer, *J. Organomet. Chem.*, **66**, 29 (1974); (j) L. H. Sommer and J. McLick, *ibid.*, **101**, 171 (1975); (k) C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, **96**, 614 (1974).

[4] P. G. Mahaffy, R. Gutowsky, and L. K. Montgomery, *J. Am. Chem. Soc.*, *102*, 2854 (1980).

[5] (a) A. K. Maltsev, V. N. Kabashesku, and O. M. Nefedov, *Dokl. Akad. Nauk SSSR*, **233**, 431 (1977); (b) O. L. Chapman, C. C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tumey, *J. Am. Chem. Soc.*, **98**, 7844 (1976); (c) M. R. Chedekel, M. Skoglund, R. L. Kreeger, and H., Schehter, *ibid.*, 7846 (1976); (d) L. E. Gusel'nikov, V. V. Volkova, V. G. Avakyan, and N. S. Nametkin, *J. Organomet. Chem.*, **201**, 137 (1980).

[6] T. Koenig and W. McKenna, *J. Am. Chem. Soc.*, **103**, 1212 (1981).

[7] (a) A. G. Brook, *Chem. Eng. News*, **59**, 18 (1981); (b) A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. Krishna, M. R. Kallury, Y. C. Poon, Y.-M. Chang, and W. Wong-Ng, *J. Am. Chem. Soc.*, **104**, 5667 (1982).

[8] L. E. Gusel'nikov, K. S. Konobeevsky, V. M. Vdovin, and N. S. Nametkin, *Dokl. Akad. Nauk SSSR*, **235**, 1086 (1977).

[9] (a) R. Walsh, *J. Organomet. Chem.*, **38**, 245 (1972); (b) R. Walsh, *Acc. Chem. Res.*, **14**, 246 (1981).

[10] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

[11] (a) W. J. Pietro, S. K. Pollack, and W. J. Hehre, *J. Am. Chem. Soc.*, **101**, 7126 (1979); (b) W. J. Pietro and W. J. Hehre, *ibid.*, **104**, 2797 (1982). The latter paper also contains determinations of the heats of formation and π bond strengths in the analogous germanium- tin- and lead-containing compounds.

[12] M. Hanamura, S. Nagase, and K. Morokuma, *Tetrahedron Lett.*, **22**, 1813 (1981).

[13] R. Ahlrichs and R. Heinzmann, *J. Am. Chem. Soc.*, **99**, 7452 (1977).

[14] Other related theoretical work includes: (a) H. B. Schlegel, S. Wolfe, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 246 (1975); (b) O. P. Strausz, L. Gammie, G. Theodorakoupoulos, P. G. Mezey, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **98**, 1622 (1976); (c) D. M. Hood, and H. F. Schaefer, III, *J. Chem. Phys.*, **68**, 2985 (1978).

[15] (a) T. J. Drahnak, J. Michl, and R. West, *J. Am. Chem. Soc.*, **103**, 1845 (1981); see also: (b) T. J. Drahnak, J. Michl, and R. West, *ibid.*, **101**, 5427 (1979).

0002-7863/83/1505-0016$01.50/0

warming of **3** in the hydrocarbon matrix (but not in argon) leads to rapid reversion to **4**. This latter result implies that the silylene is thermodynamically the more stable of the two and that the barrier to interconversion, **3** → **4**, is small, i.e., <5 kcal mol^{-1}. Work by Conlin and Wood on the low-pressure pyrolysis of 1-methylsilacyclobutane provides additional support for such an hypothesis.[16] These authors have noted trapping products of dimethylsilylene and have interpreted their findings in terms of rapid thermal isomerization from initially formed **3**.[17] Parallel experiments involving pyrolysis of 1,1-dimethylsilacyclobutane and initial formation of **1** failed to uncover evidence for reactions of an isomeric (ethyl, methyl) silylene.

Complicating what appears to be a simple matter are recent theoretical calculations on closely related systems, silaethylene and methylsilylene,[18] the results of which suggest that **3** and **4** are of nearly equal stability. This is consistent with the reported thermodynamics of isomerization. However, the calculational studies of Yoshioka annd Schaefer[18a] challenge the notion that interconversion proceeds with only slight activation and instead suggest a rather sizable barrier of 41 kcal mol^{-1} to the proposed isomerization. This is an order of magnitude too large to fit the interpretation of thermal reversion of **3** to **4** at 100 K.

We report here a direct experimental determination of the heats of formation of 1-methylsilaethylene, **3**, and dimethylsilylene, **4**, by ion cyclotron double resonance spectroscopy.[19,20] Our results show that the silaolefin, **3**, is ~28 kcal mol^{-1} more stable than the isomeric silylene, **4**, in direct contradiction to both previous experimental and theoretical work. Indirectly they also suggest a sizable barrier to interconversion of the two, in qualitative agreement with the theoretical calculations of Yoshioka and Schaefer.[18a]

Results an Discussion

The predominant ion–molecule reactions which occur when a mixture of N_2, $(CH_3)_2SiD_2$, and some base, B, of known proton affinity (in approximate ratio 50:1:1 and total pressure (3×10^{-5} torr)) are introduced into an ion cyclotron resonance spectrometer are shown in Scheme I.

Table I. Thresholds for Proton and Deuteron Abstraction from $(CH_3)_2SiD^+$

base	ΔH protonation (rel to NH_3)[a]	double resonance with BH^+	double resonance with BD^+
tetrahydrofuran	2.1	no	no
n-Pr_2CO	1.3	no	no
i-Pr_2CO	0.4	no	no
NH_3	0.0	yes	no
Et_2S	−0.4	yes	no
i-Pr_2O	−0.8	yes	no
2-fluoropyridine	−6.6	yes	no
$Me_2(i\text{-}Pr)N$	−26.1	yes	no
quinuclidine	−28.1	yes	no
Et_3N	−28.5	yes	yes
n-Pr_3N	−30.6	yes	yes
i-$Pr_2(Et)N$	−31.1	yes	yes

[a] From R. W. Taft in "Proton Transfer Equilibria", E. F. Caldin and V. Gold, eds., Wiley-Halstead, New York, 1975, p 31. The tabulated proton affinities have been slightly modified to account for higher ambient temperatures in the ICR spectrometer than previously believed.

Electron impact on $(CH_3)_2SiD_2$ leads to loss of D^-, thereby giving rise to $(CH_3)_2SiD^+$. In the presence of a sufficiently strong base, abstraction of either the carbon-bound proton or silicon-bound deuteron may occur, leading to the formation of BH^+ or BD^+ and concurrently to the production of 1-methylsilaethylene or dimethylsilylene. Therefore, the enthalpy of carbon deprotonation and silicon dedeuteration may be determined[21,22] by using a series of abstracting bases of known and increasing strength and by monitoring the onset of production of BH^+ and BD^+. Proton and deuterium incorporation due to reaction with fragment ions is precluded by double resonance experiments.[20,23] Specifically the intensity of the ion of mass corresponding to BH^+ and BD^+ was observed to decrease in response to ejection of $(CH_3)_2SiD^+$ from the system. For each base B, the total pressure of the reactant mixture was increased (by increasing the amount of nitrogen) until the observed double resonance spectrum was no longer altered. This indicates that the reactant ions have undergone sufficient collisions and are vibrationally relaxed. A selection of the bases used in this study, their gas-phase proton affinities relative to ammonia, and the results of double resonance experiments is provided in Table I.

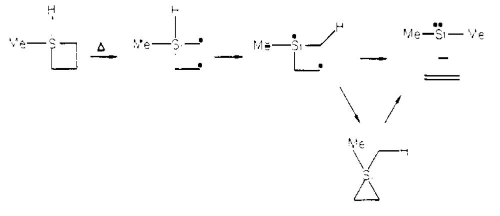
The proton affinity data, in conjunction with the heat of formation of the intermediate dimethylsilyl cation, enable the determination of heats of formation for both products. Note also that the difference in deprotonation and dedeuteration thresholds corresponds to the difference in thermochemical stabilities of 1-methylsilaethylene and dimethylsilylene, without reference to any other thermochemical data. Small effects due to isotopic substitution will tend to be canceled by similar effects arising from deuteration of the abstracting base. The overall differential isotope effect, therefore, will be small (on the order of a few tenths of kcal mol^{-1}) and has been ignored in our treatment.

i-Pr_2CO (ΔH of protonation = 0.4 kcal mol^{-1} relative to ammonia) was the strongest base considered for which carbon deprotonation was not observed. Ammonia (ΔH = 0.0 kcal mol^{-1}) was the weakest base tested which did result in deprotonation, as evidenced by the production of an ion of mass corresponding to the molecular formula NH_4^+. The average of these two values (0.2 kcal mol^{-1}) combined with the absolute enthalpy of protonation of ammonia (205 kcal mol^{-1})[24] and heats of formation of

---

[16] (a) R. T. Conlin and D. L. Wood, *J. Am. Chem. Soc.*, **103**, 1843 (1981); see also: (b) V. N. Auner and J. Grobe, *Z. Anorg. Allg. Chem.*, **459**, 15 (1979).

[17] Note, however, the recent suggestion of Barton and co-workers (T. J. Barton, S. A. Burns, and G. T. Burns, *Organometallics*, **1**, 210 (1982), and ref 8 therein) that silylene formation from pyrolysis of 1-methylsilacyclobutane may occur without the formation of 1-methylsilaethylene via initial CC rather SiC bond cleavage. The resulting biradical could then undergo a 1,2 hydride shift, followed by either direct extrusion of ethylene, leaving dimethylsilylene, or closure to an intermediate silcyclopropane which itself could then eliminate the olefin.



[18] (a) Y. Yoshioka and H. F. Schaefer III, *J. Am. Chem. Soc.*, **103**, 7366 (1981); see also: (b) J. D. Goddard, Y. Yoshioka, and H. F. Schaefer, III, *ibid.*, **102**, 7644 (1980); (c) H. J. Köhler and H. Lischka, *J. Am. Chem. Soc.*, **104**, 5884 (1982), (d) J. A. Pople, private communication. We thank Professor Pople for permission to quote unpublished data in advance of publication.

[19] In addition to that reported in ref 11, earlier related work from our laboratory includes: (a) *o*-benzyne S, K. Pollack and W. J. Hehre, *Tetrahedron Lett.*, 2483 (1980); (b) *o*- and *p*-xylylene, S. K. Pollack, B. C. Raine, and W. J. Hehre, *J. Am. Chem. Soc.*, **103**, 6308 (1981); (c) methyleneimine, D. J. DeFrees and W. J. Hehre, *J. Phys. Chem.*, **82**, 391 (1978); (d) hydrogen isocyanide, C. F. Pau and W. J. Hehre, *ibid.*, **86**, 321 (1982); (e) hydroxymethylene, C. F. Pau and W. J. Hehre, *ibid.*, **86**, 1252 (1982).

[20] Principles of operation: (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr. and R. C. Dunbar, *Int. J. Mass Spectrum.* Ion phys., **7**, 471 (1971); (d) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **49**, 111 (1978).

[21] The principal assumption made here is that thermoneutral or exothermic proton-transfer processes will be observed and that endothermic reactions will not. It is likely, however, that slightly endothermic reactions will occur to sufficient extent as to be detected. We suspect that a 2 kcal mol^{-1} error bound is large enough to account for any uncertainity in the established transfer threshold.

[22] Note that the ability to observe independent deprotonation and dedeuteration thresholds precludes the possibility of label scrambling.

[23] D. J. DeFrees, W. J. Hehre, R. T. McIver, Jr., and D. H. McDaniel, *J. Phys. Chem.*, **83**, 232 (1979).

dimethylsilyl cation (180 kcal mol^{-1})[25] and H^+ (367.2 kcal mol^{-1})[26] yields a value of 18 kcal mol^{-1} for the heat of formation of 1-methylsilaethylene. This is in reasonable accord with Walsh's estimate of 23 ± 5 kcal mol^{-1}.[9b]

A π bond energy of 42 kcal mol^{-1} for 1-methylsilaethylene may be obtained as the difference between the heat of formation of the silaolefin and that for its corresponding biradical, $\mathrm{Me(H)Si\cdot{-}CH_2\cdot}$. While the latter quantity is not known experimentally, a value of 60 kcal mol^{-1} may be estimated by combining the heats of formation of the dimethylsilane[9b] and H·[26] with its Si–H[9b] and C–H bond dissociation energies:

$$\Delta H_f(\mathrm{Me(H)Si\cdot{-}CH_2\cdot}) = D_e(\text{Si–H}) + D_e(\text{C–H}) + \Delta H_f(\mathrm{Me_2SiH_2}) - 2\Delta H_f(\mathrm{H\cdot})$$

This compares reasonably to estimates for the π bond strength in 1,1-dimethylsilaethylene.[9,11] Interestingly, the measured proton affinity of 1-methylsilaethylene is approximately 20 kcal mol^{-1} greater than that of propene, nearly identical with the suggested difference in π bond strengths between the two molecules.

Quinuclidine ($\Delta H = -28.1$ kcal mol^{-1}) was the strongest base considered for which (silicon) dedeuteration was not observed. Triethylamine ($\Delta H = -28.5$ kcal mol^{-1}) was the weakest base considered which did result in dedeuteration, as evidenced by the production of an ion of mass corresponding to the molecular formula $(C_2H_5)_3ND^+$. As before, we assign the mean (−28.3 kcal mol^{-1}) as the actual threshold; this leads to a heat of formation of dimethylsilylene of 46 kcal mol^{-1}. While this is in good accord with a value of 44 kcal mol^{-1} obtained by Neudorfi and Strausz from rate data on the pyrolysis of dimethylsilane, it is in poor agreement with Walsh's estimate of 26 kcal mol^{-1} for $\Delta H_f(298)$ for the species.[9b]

The present heats of formation of both 1-methylsilaethylene and dimethylsilylene depend directly on the heat of formation of their common precursor, dimethylsilyl cation. Any error in thermochemistry here leads to an equal error for the two neutrals. Note, however, that the observed 28 kcal mol^{-1} difference in the proton and deuteron abstraction thresholds yields directly, and without reference to any other thermochemical data, the difference in stabilities of 1-methylsilaethylene and dimethylsilylene; the former is the more stable. Our data disagree both with the experiments of Drahnak, Michl, and West[15] and of Conlin and Wood,[16] which suggest an opposite ordering of stabilities, and with the quantum chemical calculations of Schaefer,[18a] Köhler and Lischka,[18c] and Pople,[18d] which depict isomers of nearly equal stability.

Note also that our data provide indirect support for the notion that interconversion of 1-methylsilaethylene and dimethylsilylene proceeds only with significant barrier, as the theoretical calculations of Schaefer and his co-workers suggest.[18a,b] The fact that independent proton and deuteron thresholds are observed implies to us a significant barrier to isomerization. Previous ICR experiments with the hydrogen cyanide–hydrogen isocyanide[19d] and formaldehyde–hydroxymethylene[19e] tautomeric equilibria, both of which are known from theory to involve high interconversion barriers,[28] also revealed distinguishable thresholds. On the other hand, efforts to generate the trimethylenemethane biradical in the gas phase[29] lead instead (apparently) to methylenecyclopropane, consistent with theoretical work which shows a barrier of only a few kcal mol^{-1}.[30]

The disagreement of the present experimental thermochemical results with the high-level quantum chemical calculations of Schaefer, Köhler and Lischka and of Pople[18] is particularly disturbing. It is possible, although it does not seem likely, that our data might lend itself to alternative interpretation. Reasonable possibilities include the existence of a sizeable barrier to dedeuteration of dimethylsilyl cation, preferential formation of excited-state (triplet) as opposed to ground-state (singlet) dimethylsilylene or generation of yet another C_2H_6Si isomer. It is also conceivable that the theoretical calculations on these silicon-containing species are not as reliable in their prediction of relative thermochemical stabilities as experience, wholly with molecules containing first-row elements, suggests. Further experimental and/or theoretical work seems to be required.

Registry No. 3, 38063-40-0; **4**, 6376-86-9; $(CH_3)_2SiD_2$, 1066-41-7.

---

[24] (a) The original value of 202.3 kcal mol^{-1} for the proton affinity of the ammonia standard as derived from ICR spectroscopy, (J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.* **99**, 5417 (1977)) has been revised upward to 205 kcal mol^{-1} due to recent work; (b) 203.6 kcal mol^{-1}, S. T. Ceyer, P. W. Tiedemann, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, **70**, 14 (1979); (c) 207 kcal mol^{-1}, F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 4067 (1979); (d) 209.2 kcal mol^{-1}, R. G. McLoughlin and J. C. Traeger, *ibid.*, **101**, 5791 (1979).

[25] Averaged from the appearance potentials of dimethylsilane and trimethylsilane (H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, **6** (1977)) and their heats of formation.[9b]

[26] D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*), **37** (1971).

[27] P. S. Neudorfi and O. P. Strausz, *J. Phys. Chem.*, **82**, 241 (1978).

[28] See ref 19d and 19e for references to theoretical work on barrier heights.

[29] C. F. Pau, W. J. Hehre, and P. Dowd, unpublished results.

[30] W. J. Hehre, L. Salem, and M. R. Willcott, *J. Am. Chem. Soc.*, **96**, 4328 (1974).

Mechanism of Iron Dissolution and Passivation in an Aqueous Environment: Active and Transition Ranges

Alfred B. Anderson* and N. C. Debnath

Contribution from the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106. *Received July 1, 1982*

Abstract: Structures and stabilities of FeOH, $(FeOH)^+$, $FeOH(H_2O)_5{}^+$, $Fe(OH)_2$, $Fe(OH)_2(H_2O)_4$, $Fe(H_2O)_6{}^{2+}$, and $Fe(H_2O)_6{}^{3+}$ are determined and analyzed using an atom superposition and electron delocalization (ASED) molecular orbital theory. The bonding of an Fe atom, FeOH, and $Fe(OH)_2$ to an Fe(100) surface is compared and contrasted. The theory supports a surface iron dissolution mechanism where, at sufficiently anodic potentials, surface FeOH species desorb as $(FeOH)^+$ and are solvated as $FeOH(H_2O)_5{}^+$. Evidence is presented for the precipitation of solid $Fe(OH)_2$ formed by hydrolysis of $FeOH(H_2O)_5{}^+$.

Introduction

A protective passive film of approximately 40 Å thickness forms on ferrous metals exposed to the atmosphere. An understanding of the passive film's mechanism of formation, structures, and failures due to active anions such as chloride has been sought for many years.[1]

0002-7863/83/1505-0018$01.50/0