

Figure 3. Plot of dipolar correlation time vs. viscosity for $Cu(H_2O)_{\delta^{2+}}$ in water-glycerin mixtures.

whose slope can be used to calculate a should result. Values of τ_c for Cu(H₂O)₆²⁺ in water-glycerin solutions were calculated from eq 1 by the following procedure. Values of ω_s corrected to 60 Mc/sec and τ_c at 40° in pure water were obtained from previous investigations.^{5,8} The value of P was calculated by assuming a coordination number of 6. A value of the constant Cwas obtained and subsequently used to calculate τ_{0} in water glycerin solutions. This procedure was adopted to avoid calculating C from first principles, since it contains a R^{-6} (R = ion-proton internuclear distance) dependence and R is not accurately known. The resulting excellent linear plot is given in Figure 3. A least-squares treatment of the slope gives a value of a =2.3 Å, which is in as good agreement, as can be expected, with previously suggested values of R of 2.5^{20} and 2.8 $Å.^5$ A macroscopic solvent continuum model (eq 2) appears to do a surprisingly good job of accounting for the data, in view of obvious difficulties which result if a microscopic picture is considered.^{21,22}

Acknowledgment. This investigation was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. 212-65. I wish to thank Dr. T. R. Stengle and Dr. C. H. Langford for many helpful discussions and the reading of the manuscript.

(20) N. Bloembergen, Physica, 16, 95 (1950).

(21) S. Broersma, J. Chem. Phys., 24, 659 (1955).

(22) L. S. Frankel, T. R. Stengle, and C. H. Langford, Chem. Commun., 393 (1965).

Pyrolysis and Energetics of Halocarbons in Cryochemical Studies of Divalent Carbon^{1a}

by W. J. Martin^{1b,c} and H. A. McGee, Jr.

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332 (Received July 7, 1967)

Diffuorocarbene is unusually unreactive in the gas phase, presumably due to its singlet electronic ground state,² the electronegativity of the fluorine atoms,³ and the favorable contributions of resonance structures.⁴ Although it has not been observed, diiodocarbene may be additionally unreactive due to steric shielding of the carbon by the enormous iodine atoms. Consequently, as part of a continuing study of the preparation and properties of unusual reagents (not trapped free radicals) by cryochemical procedures, it has seemed reasonable to explore the stability and reactivity of CF_2 and CI_2 at very low temperatures. In related earlier experiments, CCl₂ was ostensibly prepared as a stable yellow solid melting at -114° and boiling at -20° by means of a liquid air quench of the effluent from the low-pressure pyrolysis of CCl₄ in a graphite tube at 1300°,5 but this product substance was later shown to be an equimolar mixture of C₂Cl₂ and Cl₂.⁶ Studies with the related molecule, SiF₂, which has a half-life of 150 sec in the gas phase at 0.1 torr and 25°, have been more fruitful.⁷

The primary analytical tool in this study was the Bendix time-of-flight mass spectrometer and cryogenically cooled inlet system⁸ which usually permits the identification of species regardless of their stability even at very low temperatures.

A number of halocarbons were pyrolyzed either in a tubular monel furnace or on heated filaments of platinum and tungsten. Calculations indicated that the furnace pyrolyses should have attained equilibrium. An essentially collision-free path between the pyrolysis and the ion source was necessary, and this was accomplished in the usual way by the use of low pressures, close spacing, and differential pumping. The filaments and the furnace outlet were positioned 3/8 and 1/8 in., respectively, from the ionizing electron beam. Furnace temperatures were limited to 500°, but the filaments were usable up to temperatures at which they collapsed. Ionization occurred with tungsten filaments either on the hot metal surface or from the acceleration of the surrounding electron cloud by the potential between opposite ends of the filament, but these ions were readily biased out of the pyrolysis products before

(3) J. P. Simons and A. J. Yarwood, Nature, 192, 943 (1961).

- (5) M. Schmeisser and H. Schröter, Angew. Chem., 72, 349 (1960).
- (6) M. Schmeisser, H. Schröter, H. Schilder, J. Massonne, and F. Rosskopf, Ber., 95, 1648 (1962).
- (7) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, J. Am. Chem. Soc., 87, 2824 (1965).
- (8) H. A. McGee, Jr., T. J. Malone, and W. J. Martin, Rev. Sci. Instr., 37, 561 (1966).

^{(1) (}a) The authors gratefully acknowledge support of this research byNASA Grant NsG-123-61; (b) abstracted from a thesis presented by W. J. M. in partial fulfillment of his requirements for the Ph.D. degree in Chemical Engineering, March 1965; (c) W. J. M. expresses appreciation to NSF for a Cooperative Graduate Fellowship during 2 years of graduate study.

⁽²⁾ F. X. Powell and D. R. Lide, Jr., J. Chem. Phys., 45, 1067 (1966).

⁽⁴⁾ J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, p 40.

, i i i i i i i i i i i i i i i i i i i			
	This work,		
Parent compound	Ion	eV	Lit., eV
CF,I	CF ₂ I+	10.3 ± 0.2	10.0 ± 0.3^{a}
	CF ₃ +	11.1 ± 0.2	11.28 ± 0.2^{b}
	CF_2^+	17.1 ± 0.1	18.5 ± 0.6^{a}
	I+	12.9 ± 0.2	$12.9 \pm 0.15^{\circ}$
			13.6 ± 0.5^{a}
CF ₂ from pyrolysis	CF_2 +	11.8 ± 0.1	11.7^{d}
of CF ₃ I	-		11.86 ± 0.1^{11}
I ₂ from pyrolysis	I+	8.8 ± 0.1	$8.62 \pm 0.06^{\circ}$
of CF ₈ I			
c-CaF8	CF_2^+	19.0 ± 1.0	
C ₂ F ₄ from pyrolysis	CF_2^+	15.0 ± 1.0	15.26 ± 0.05^{11}
of c -C ₄ F ₈	_		
CHClF ₂	CHClF ₂ +	12.3 ± 0.1	$12.69 \pm 0.15^{\prime}$
	CHF ₂ +	12.8 ± 0.1	$12.59 \pm 0.15'$
CF.ClCOOH	CF_2^+	13.4 ± 0.1	
CHI3	CHI _s +	9.4 ± 0.2	
	CHL+	10.0 ± 0.1	

Table I: Appearance Potentials

^a V. H. Dibeler, R. M. Reese, and F. L. Mohler, J. Res. Natl. Bur. Std., 57, 113 (1956). ^b J. Marriott, quoted by C. R. Patrick, "Advances in Fluorine Chemistry," M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Vol. 2, Butterworth and Co., Ltd., London, 1961, p 17. ^c J. B. Farmer, I. H. S. Henderson, F. P. Lossing, and D. G. H. Marsden, J. Chem. Phys., 24, 348 (1956). ^d I. P. Fisher, J. B. Homer, and F. P. Lossing, J. Am. Chem. Soc., 87, 957 (1965). ^e D. C. Frost and C. A. McDowell, "Advances in Mass Spectrometry," J. Waldron, Ed., Pergamon Press, New York, N. Y., 1959, p 427. ^f D. L. Hobrock and R. W. Kiser, J. Phys. Chem., 68, 575 (1964). Related data on CF₃I also appear in F. H. Dorman, J. Chem. Phys., 41, 2857 (1964).

they entered the source. The appearance potentials of some of the principal ions from the products of these pyrolyses were measured using the retarding potential difference technique,⁹ and a summary of the results of those measurements appears in Table I.

 $CF_2ClCOOH$ has been shown to be a useful source of CF_2 for liquid phase organic reactions,¹⁰ but CF_2 was not detected from the pyrolysis of the acid at temperatures of up to 500° even though severe decomposition did occur. The ionization efficiency data for $A(CF_2^+)$ indicated the formation of an excited ion at the same energy above the ground state ion (within experimental error) as was observed in the determination of $I(CF_2)$.

 $c-C_4F_8$ was pyrolyzed on platinum filaments at 1100° to produce a lowering of $A(CF_2^+)$ from approximately 19 to 15 eV, indicating decomposition into $C_2F_4(A(CF_2^+))$ from $C_2F_4 = 15.26 \pm 0.05 \text{ eV}$).¹¹ At 1600°, the CF_2^+ signal responded to RPD change at still lower energies, but the intensity was too low for confirmation from ionization efficiency studies. Pyrolysis on tungsten gave a similarly weak indication of the presence of free CF_2 . CF_2 is produced by the pyrolysis of C_2F_4 in a graphite furnace at 1300°.¹¹

 $CHClF_2$ was pyrolyzed on both tungsten and platinum filaments and in furnaces, but free CF₂ was not observed. Furnace pyrolysis at up to 500° produced little change in the mass spectrum except for the expected sharply decreased parent ion intensity. The values of $A(CHF_2^+)$ and $A(CHF_2Cl^+)$ from CHClF₂ reported in Table I may be compared with those reported by Hobrock and Kiser, who recognized the improbability of their inverted relative magnitudes. CF_2CFCl was pyrolyzed in furnaces and on tungsten filaments without producing free CF₂. Pyrolysis on platinum filaments above 1000° yielded meager but equivocal evidence for the presence of CF₂.

 C_2I_4 was pyrolyzed at 100–300° in the furnace inlet, but C_2I_2 and I_2 rather than CI_2 were formed, even at the lowest usable temperatures.

 CHI_3 was pyrolyzed in the furnace inlet at temperatures up to 300°, but free CI₂ was not observed. The value of $I(CHI_3)$ suggests ionization from a nonbonding orbital of an iodine atom since it corresponds so closely to the ionization potential of other iodine-containing compounds, e.g., $I(CH_3I) = 9.55 \text{ eV}^{12}$ and $I(I_2) =$ 9.41 eV.¹²

 $CF_{3}I$ dissociated to yield free CF_{2} upon passing over an incandescent platinum filament at 1100°. $A(CF_{2}^{+})$ from $CF_{3}I$ at room temperature was 17.1 \pm 0.1 eV, but upon filament pyrolysis, CF_{2}^{+} appeared at its ionization potential. A sharp break in the ionization efficiency data at 12.8 eV evidently corresponds to the formation of CF_{2}^{+} in an excited state. Pyrolyses of $CF_{3}I$ on tungsten filaments at 1000–1700° and in a monel furnace at 100–500° failed to produce CF_{2} . Pyrolysis of fluorocarbons on platinum filaments poisoned the wire making it ineffective in producing CF_{2} in subsequent pyrolyses of $CF_{3}I$. Prominent features, other than CF_{2} , in the mass spectrum of $CF_{3}I$ upon

⁽⁹⁾ C. E. Melton and W. H. Hamill, J. Chem. Phys., 41, 546 (1964).
(10) Reference 4, p 47.

⁽¹¹⁾ R. F. Pottie, J. Chem. Phys., 42, 2607 (1965).

⁽¹²⁾ F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p 113.

platinum filament pyrolysis were (1) a large increase in IF⁺ relative to the parent ion, (2) the appearance of C_2F_4 , C_2F_6 , and I_2 , and (3) the absence of free CF₃. The CF₃ free radical, which was expected in view of earlier related work,^{1b} was not detected by the appearanc₃ potential technique in any of these experiments with CF₃I. The presence of I_2 in the products prevented the detection of free I atoms since $A(I^+)$ from I_2 is less than I(I) due to pair production. Although neither was detected, the presence of both CF₃ and I at some point in the process seems reasonable since both C_2F_6 and I_2 were identified as major contributors to the mass spectra of the products. CF₃ was not lost by the reaction, $2CF_3 \rightarrow C_2F_4 + F_2$, since F_2 was absent, but its reaction to form CF₂ and CF₄ is a possibility.

Using $I(CF_3) = 9.25 \text{ eV}$,¹³ $D(F_3C-I) = A(CF_3^+) - I(CF_3) = 11.1 - 9.25 = 1.85 \text{ eV}$ or 43 kcal/mole, whereas employing $A(I^+)$ yields $D(F_3C-I) = A(I^+) - I(I) = 12.9 - 10.45 = 2.45$ or 57 kcal/mole. This latter value is surprisingly close to the average energy of the C-I bond in CI₄ of 57.4 kcal/mole¹⁴ and to the energy of the C-I bond in CH₃I of 55 kcal/mole.¹⁵ The I⁻ ion from CF₃I appears at essentially zero electron energy,¹⁵ and hence $D(F_3C-I)$ can be no greater than EA(I) of 3.14 eV. $A(I^+)$ from CF₃I may be too large since usually only the fragment with the smaller ionization potential is formed without excess kinetic energy,¹⁶ and here I(I) is 1.2 eV greater than $I(CF_3)$.

Having thus demonstrated that CF_2 was produced, the filament pyrolysis was conducted inside a cryogenically cooled reactor-inlet system.⁸ Argon was used as a carrier to sweep the pyrolysis products away from the filament and down a monel condensation tube thermostated at 77°K which successfully condensed all of the products. The cold composite solid was then slowly warmed, the spectra of the evolved gases were recorded as a function of temperature, and a discriminating low-energy electron beam was employed to search for free CF_2 or CF_3 in the evolved gases. The cold sample emerged from the refrigerated inlet system directly into the electron beam of the ion source. The major products were CF4, C2F4, C2F6, and the unchanged parent, $CF_{3}I$, which appeared in the order given, *i.e.*, in the order of decreasing volatilities. The results were the same when the condensation tube was cooled to 4.2° K. In no experiment was free CF₂ or CF₃ or any other unusual or reactive molecule observed. An earlier matrix experiment indicated that CF₂ dimerized at 14°K in dilute solutions in argon,¹⁷ while another suggested that CF_2 existed in fluorocarbon matrices at up to 95° K, while CF₃ existed at up to 107°K.¹⁸ In the present study, if we make the reasonable assumption that the CF_2 survived the quench, it is clear that it is lost in this rather complex matrix at temperatures below that at which it can exert the minimum required vapor pressure of 3×10^{-6} torr that is characteristic of the cryogenic inlet system.

Notes

Hence, we conclude that the extraordinary half-life of singlet CF_2 in the gas phase is due to factors not implying the existence of an activation energy for its dimerization, and the possibility of the existence of CF_2 as a cryochemical reagent must be dismissed. The situation with CI_2 remains uncertain since this species has not yet been observed. The search for compounds of divalent carbon or divalent silicon which will be preparable as cryochemical reagents is continuing.

(13) C. Lifshitz and W. A. Chupka, J. Chem. Phys., in press. We thank Dr. Chupka for kindly providing a preprint of this paper.

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 85.

(15) V. H. Dibeler and R. M. Reese, J. Res. Natl. Bur. Std., 54, 127 (1955).

(16) D. P. Stevenson, Discussions Faraday Soc., 10, 35 (1951).

(17) D. E. Milligan, D. E. Mann, M. E. Jacox, and R. A. Mitsch, J. Chem. Phys., 41, 1199 (1964).

(18) S. V. R. Mastrangelo, J. Am. Chem. Soc., 84, 1122 (1962).

The Anion and Cation Radicals of

N,N-Dimethyl-*p*-nitroaniline

by R. F. Nelson and R. N. Adams

Department of Chemistry, University of Kansas, Lawrence, Kansas 66044 (Received July 18, 1967)

There is ample evidence that the anion and cation radicals of the same alternant hydrocarbons possess very similar electron paramagnetic resonance (epr) spectra¹⁻⁴ with respect to coupling constants of the various nuclei and the over-all spectral widths. The epr spectra of cation and anion radicals of nonalternant hydrocarbons are, as expected, dissimilar due to different spin populations in the two frontier orbitals.⁵⁻⁷ Coupling constants of corresponding nuclei in the anion and cation radicals are not comparable and spectral widths vary considerably. In both cases (for alternant and nonalternant radicals), the cation spectral width is generally the larger, but the opposite is sometimes true.^{5,6} Brown and Karplus have found⁸ that valencebond spin-density calculations at least partially account for slightly larger cation radical spectra in some alter-

(1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 159-163.

 (2) (a) L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, J. Phys. Chem., 70, 404 (1966); (b) ibid., 71, 2223 (1967).

(3) I. C. Lewis and L. S. Singer, J. Chem. Phys., 43, 2712 (1965).
(4) A. Carrington, F. Dravnieks, and M. C. R. Symons, J. Chem. Soc., 947 (1959).

- (5) F. Gerson and J. Heinzer, Chem. Commun., 488 (1965).
- (6) F. Gerson and J. Heinzer, Helv. Chim. Acta, 49, 7 (1966).
- (7) I. C. Lewis and L. S. Singer, J. Chem. Phys., 44, 2082 (1966).
- (8) T. H. Brown and M. Karplus, ibid., 46, 870 (1967).