field from $CFCl_3$ with an area ratio of 6:1 (lit. for $(CF_3)_2CFCF(CF_3)_2$: bp 58.5–59.0° (741 mm),[2] 60.0° (756 mm);[3a] ir max 1299, 1277, 1149, 1009, 980, 961, 892, 747, and 722 cm^{-1} [3b]).

Perfluoro-2-methyl-2-pentene, $CF_3CF_2CF{=}C(CF_3)_2$,[4] bp 50.5°, 0.040 mol, was added to 0.040 mol of AgF in 100 ml of CH_3CN during 1 hr with solution of the AgF to form perfluoro-1,1-dimethylbutylsilver, $CF_3CF_2CF_2C(CF_3)_2Ag$. The addition of HCl yielded 0.025 mol of $CF_3CF_2CF_2CH(CF_3)_2$, ir max (gas) 2985 (C–H), with strong absorption at 1358, 1288, 1240, 1210, and 1111 cm^{-1}, determined by glpc and isolated by drowning in water, followed by distillation and preparative glpc. The glpc retention times and infrared spectrum found for $CF_3CF_2CF_2CH(CF_3)_2$ were identical with those of an authentic sample.[5] A second preparation of $CF_3CF_2CF_2C(CF_3)_2Ag$ with 0.100-mol quantities yielded, after treatment of the filtered reaction product with bromine, 0.094 mol of AgBr and 0.060 mol of $CF_3CF_2CF_2CBr(CF_3)_2$: bp 97.5° (745 mm); mass spectrum (high resolution), molecular ion at 399.8970 ($C_6{}^{79}BrF_{13}$, 399.8954); nmr (^{19}F) 62.5, 77.8, 100.5, and 116.3 ppm upfield from CCl_3F with area ratios of 6:3:2:2; ir max (strong) 1342, 1245–1300 (complex), 1130, 964, 931, 825, 735, and 713 cm^{-1}.

The above perfluoroalkylsilver compounds can also be conveniently prepared in sealed-glass ampoules. Using this technique a slow partial reaction was observed between $CF_3CF{=}CFCF_3$ and AgF in CH_3CN; $CF_2{=}CClF$ and $CF_2{=}CCl_2$ also gave as yet uninvestigated products. On the other hand, 2-chloroperfluoropropene added AgF in CH_3CN more rapidly than $CF_3CF{=}CF_2$, a result consistent with the expected greater stabilization of an "anionic" transition state by α-Cl as compared with α-F.[6] Treatment of the filtered $(CF_3)_2CClAg$[7] solution with bromine in CH_3CN yielded 73% C_3BrClF_6, bp 50.2–51.0° (743 mm); mass spectrum (high resolution), molecular ion at 263.8775 ($C_3F_6{}^{35}Cl^{79}Br$, 263.8775); ir max (strong) 1275, 1251, 1240, 936, 882, 748, and 707 cm^{-1} (lit.[8] for $CF_3CBrClCF_3$: bp 51–52°). Thermal decomposition of $(CF_3)_2CClAg$ at 100° was shown to form $(CF_3)_2CClCCl(CF_3)_2$, mp 92.1–93.5° (lit.[2b] mp 91.5–93.0°). Solutions of perfluoroisopropylsilver were also prepared in "tetraglyme," dimethylformamide, and benzonitrile using sealed ampoules. It was found that benzene, ethyl ether, and tetrahydrofuran could be added in large amounts to $(CF_3)_2CFAg$ in acetonitrile solution without the formation of a precipitate.

The formulation of the perfluoro olefin–silver fluoride addition products as perfluoroalkylsilvers is supported by the experimental results cited above, by the electron-deficient character of the fluoro olefins, and by previous observations on their addition reactions with metal fluorides. Such addition reactions to form fluorocarbanions reversibly as reaction intermediates were first observed with potassium fluoride, *i.e.*, the formation of fluoroalkylpotassiums,[9] and the prediction of a considerable chemistry for such ionic intermediates has been substantiated.[10] The order of reactivity for perfluoro olefins with silver fluoride in acetonitrile appears to be the same as that found with cesium and potassium fluorides.[4b] In anhydrous hydrogen fluoride, a solvent in which fluoride ion is unreactive but in which silver ion is a highly effective π-bonding reagent,[11] silver fluoride reacts only slowly with perfluoropropene at 125°.[12]

By comparison with the corresponding perfluoroalkylcesiums the perfluoroalkylsilver compounds described above are stable and covalent.[13] They do not readily transfer $R_F{}^-$ groups to sp^2 carbon or revert to metal fluoride and olefin.[14] They decompose homolytically at convenient temperatures. We believe that our observations with the silver compounds point to the synthesis of other fluoro organometallic compounds by addition of metal fluorides to fluoro olefins and to a significant new free-radical chemistry for such systems.

Acknowledgment. This work was supported by a grant from the National Science Foundation for which grateful acknowledgment is made.

---

(2) M. Prober, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1946. Prepared by: (a) $(CH_3)_2C{=}C(CF_3)_2 + F_2 \rightarrow (CF_3)_2CFCF(CF_3)_2$; (b) $CF_3CCl{=}CF_2 + F_2 \rightarrow (CF_3)_2CClCCl(CF_3)_2$ (W. T. Miller, Jr., in "Preparation, Properties and Technology of Fluorine and Organic Fluoro Compounds," C. Slesser and S. R. Schram, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p 678).

(3) R. D. Chambers, W. K. R. Musgrave, and J. Savory: (a) *J. Chem. Soc.*, 3779 (1961); (b) *ibid.*, 1993 (1962).

(4) (a) W. J. Brehm, K. G. Bremer, H. S. Eleuterio, and R. W. Meschke, U. S. Patent 2918501 (1959); (b) M. J. Roura (Fraticelli), Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1965.

(5) Prepared by A. B. Clayton by the reaction of KHF_2 with $CF_3CF_2CF{=}C(CF_3)_2$ in aqueous acetonitrile.

(6) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 5497 (1957); J. Hine and A. D. Ketley, *J. Org. Chem.*, **25**, 606 (1960).

(7) The possible α elimination of AgCl from chloroperfluoroalkylsilvers with transfer of methylene units such as $(CF_3)_2C$ is being investigated.

(8) B. L. Dyatkin, A. A. Gevorkyan, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1873 (1965).

(9) W. T. Miller, Jr., and J. H. Fried, 132nd National Meeting of the American Chemical Society, New York, N. Y., Abstracts, 1957, p 29M; J. H. Fried and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **81**, 2078 (1959); W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

(10) For a recent review see: J. A. Young, *Fluorine Chem. Rev.*, **1**, 359 (1967).

(11) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **79**, 2495 (1957).

(12) W. T. Miller, Jr., M. B. Freedman, J. H. Fried, and H. J. Koch, *ibid.*, **83**, 4105 (1961).

(13) A range of properties can be anticipated for the R_FAg's. No "primary" perfluoro compounds of the type R_FCF_2Ag have been prepared.

(14) The dimers and trimers which are readily formed from $CF_3CF{=}CF_2$ with CsF in CH_3CN at 25° [4b] were not significant products in the above experiments with $CF_3CF{=}CF_2$.

William T. Miller, Jr., Robert J. Burnard
Department of Chemistry, Cornell University
Ithaca, New York

Received August 9, 1968

Matrix Infrared Spectrum and Bonding in the Lithium Superoxide Molecule, LiO_2

Sir:

There has been a great deal of recent research activity on free radicals of the formula XO_2 where X = F,[1] Cl,[2] and H.[3] The bonding in these species is characterized by the O–O stretching frequencies which shift from 1495 to 1441 to 1101 cm^{-1} in the above order. Spratley and Pimentel[4] have rationalized this trend by suggesting that the X atom is bonded to an oxygen π^*

---

(1) P. N. Noble and G. C. Pimentel, *J. Chem. Phys.*, **44**, 3641 (1966); R. D. Spratley, J. J. Turner, and G. C. Pimentel, *ibid.*, **44**, 2063 (1966).

(2) A. Arkell and I. Schwager, *J. Am. Chem. Soc.*, **89**, 5999 (1967).

(3) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **38**, 2627 (1963).

(4) R. D. Spratley and G. C. Pimentel, *J. Am. Chem. Soc.*, **88**, 2394 (1966).

molecular orbital where a certain fraction of an antibonding electron is added to the O_2 molecular orbital system. In order to get a better understanding of bonding in these interesting radicals, we have prepared LiO_2 for infrared spectral study using the matrix reaction of lithium atoms and oxygen molecules.

The common oxide of lithium is lithium oxide, Li_2O, whereas atmospheric oxidation of sodium produces the peroxide, Na_2O_2, while potassium yields the superoxide, KO_2.[5] LiO_2 has been prepared by oxidizing lithium in liquid ammonia solution[6] at −78° and by vacuum drying $Li_2O_2 \cdot 2H_2O_2$ near 120°,[7] but the pure substance has not been isolated. Recent infrared studies of lithium oxides isolated the equilibrium vaporization (1600–1750°K) products of crystalline Li_2O in a krypton matrix.[8] The infrared spectrum of LiO_2 is of interest in order to characterize this molecule and to provide some insight into the bonding in normally ionic species which are isolated as molecules.

The experimental technique and apparatus have been described earlier.[9,10] Samples of oxygen ($^{16}O_2$, $^{18}O_2$, or $^{16}O_2$–$^{16}O^{18}O$–$^{18}O_2$ mixtures) in argon or krypton matrices ($M/O_2 = 100/1$ to $500/1$) or pure $^{16}O_2$ were simultaneously deposited with an atomic beam of lithium (^6Li, ^7Li, or a ^6Li–^7Li mixture; $M/Li \approx 300/1$ to $1000/1$) on a cesium iodide window maintained at 15°K. Infrared spectra were recorded in the 200–4000-cm^{-1} spectral region.

In every experiment using the inert gas matrices, four very intense absorptions appeared in the 400–900-cm^{-1} region which showed lithium and oxygen isotopic shifts. Two of these absorptions were favored at high lithium concentrations and showed a 1/2/1 intensity triplet structure when an equimolar mixture of lithium isotopes was used. This behavior is characteristic of molecules containing two equivalent lithium atoms. The remaining two very intense bands showed well-resolved doublets at 743.8 and 699.0 cm^{-1}, and 507.3 and 492.5 cm^{-1} in the mixed lithium isotope experiment, the same frequencies observed separately in single lithium isotope experiments. Furthermore, an increase in the O_2 concentration favored these bands relative to those attributed to species containing two lithium atoms, which indicates that the above vibrational absorption frequencies are due to species containing a single lithium atom.

An additional sharp band ($\nu_{1/2} = 1.2$, 0.12 OD) appearing at 1097.0 cm^{-1} using ^7Li and $^{16}O_2$ in argon shifts to 1097.5 cm^{-1} with ^6Li. The Li concentration dependence of this feature indicates its association with the single lithium atom species although it was not possible to resolve the ^6Li and ^7Li components in the mixed lithium isotopic experiment. The $^{18}O_2$ counterparts of these features appear at 1035.5 and 1036.0 cm^{-1} for ^7Li and ^6Li, respectively.

When lithium atoms are deposited in a $^{16}O_2$ matrix, the major features observed are due to the species containing a single lithium atom. When these samples are warmed to 34°K and are recooled to 15°K, the feature near 1100 cm^{-1} and the two intense bands in the lithium–oxygen fundamental region diminish in intensity by 80 ± 4% maintaining approximately constant relative intensities. Thus, the absorptions near 1100, 700, and 500 cm^{-1} are attributed to the same molecular species which contains a single lithium atom.

The structure of this species is revealed by the mixed oxygen isotopic experiments ($^{16}O_2/^{16}O^{18}O/^{18}O_2 = 1/2/1$) where each of the three bands becomes a 1/2/1 relative intensity triplet with $^{16}O_2$ and $^{18}O_2$ components appearing at the same frequencies observed in the pure oxygen isotope experiments. The 1/2/1 triplets indicate that the species of interest here contains two equivalent oxygen atoms which completes the identity of LiO_2 and indicates that the molecule has an isosceles triangular structure with equivalent oxygen atoms.

The absorption near 1100 cm^{-1} shows a very large oxygen isotopic shift and a small lithium shift which suggests its assignment as ν_1, the symmetric O–O stretch. The feature near 700 cm^{-1} shows a large lithium shift and a small oxygen shift, whereas the 500-cm^{-1} absorption shows a large oxygen isotopic effect and a relatively smaller lithium effect. This behavior is consistent with the assignment of the 700-cm^{-1} band to ν_2, the symmetric lithium–oxygen stretching mode, and the 500-cm^{-1} absorption to ν_3, the antisymmetric Li–O vibration for a triangular LiO_2 molecule in the C_{2v} point group. (The 500-cm^{-1} absorption involves two equivalent oxygen atoms; hence it cannot be a Li–O–O valence angle bending mode. No absorption was observed down to 220 cm^{-1} with isotopic structure appropriate to such a bending vibration for a bent or linear Li–O–O molecule.)

This is indeed a unique molecular structure and it merits further analysis. We have complete infrared spectra for six isotopic molecules which provide ample basis for normal coordinate calculations. The structural parameters are assumed from comparison of similar bonds: $R_{O-O} = 1.33$ Å from NaO_2 crystal,[11] $R_{Li-O} = 1.70$ which is near the 1.59 Å estimated[8] for Li_2O. A large amount of experience indicates that these calculations are not sensitive to small changes in bond distances. The three-constant potential function, $F_{O-O} = 5.53 \pm 0.08$ mdyn/Å, $F_{Li-O} = 1.175 \pm 0.015$ mdyn/Å, and $F_{Li-O,Li-O} = -0.172 \pm 0.008$ mdyn/Å, calculates the 18 frequencies with an average difference between calculated and observed of 0.7 cm^{-1}. This excellent agreement for a large number of isotopic frequencies verifies the vibrational assignments and structure of LiO_2 reported here.

Recent Raman observations of the superoxide ion in alkali halide lattices[12] predict the frequency of free O_2^- to be near 1090 cm^{-1}. This frequency gives $F_{O-O} = 5.59$ mdyn/Å for the O_2^- ion. The close agreement between the O–O force constants in LiO_2 and O_2^- suggests that the molecule LiO_2 may be completely ionic with a Li cation bonded directly to an O_2^- anion by coulombic attractive forces. The bonding of lithium to two *equivalent* oxygen atoms can best be rationalized as ionic bonding. The lithium–oxygen force constant

---

(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1966.

(6) J. K. Thompson and J. Kleinbert, *J. Am. Chem. Soc.*, **73**, 1243 (1951).

(7) I. I. Vol'nov and A. N. Shatunina, *Zh. Neorg. Khim.*, **4**, 257 (1959).

(8) D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.*, **39**, 2463 (1963); K. S. Seshadri, D. White, and D. E. Mann, *ibid.*, **45**, 4697 (1966).

9) W. L. S. Andrews and G. C. Pimentel, *ibid.*, **44**, 2361 (1966).

10) L. Andrews, *ibid.*, **48**, 972 (1968).

(11) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **72**, 2251 (1950).

(12) J. Rolfe, W. Holzer, W. F. Murphy, and J. H. Bernstein, *J. Chem. Phys.*, **49**, 963 (1968).

is less than observed for LiON (1.33 mdyn/Å),[9] LiO (1.59 mdyn/Å),[8] and Li_2O (2.0 mdyn/Å);[8] however, it is not surprising that a single lithium bonded to two oxygen atoms would have a lower force constant, as is observed for Li_2O_2 with the rhombus structure (0.56 mdyn/Å).[8]

Acknowledgment. The author gratefully acknowledges support by the National Science Foundation under Grant GP-8587.

Lester Andrews
Chemistry Department, University of Virginia
Charlottesville, Virginia
Received October 16, 1968

The Photolysis of Methane at 584 A[1]

Sir:

Recent studies from this laboratory[2–5] have demonstrated the feasibility of using conventional closed-system photolysis techniques with high-energy light sources as a means of studying the unimolecular fragmentation of parent ions and superexcited molecules, as well as the ensuing reactions of fragment ions or radicals. Such studies have been carried out using krypton[3] resonance lamps (1236 Å, 10.0 eV) and, more recently, argon resonance lamps[3–5] (1067–1048 Å, 11.6–11.8 eV) which emit photons of energy high enough to ionize most hydrocarbons. Such photons can be transmitted through ordinary lithium fluoride windows.

In order to extend such studies to still higher energies, a helium resonance lamp (584 Å, 21.2 eV) and neon resonance lamp (744 Å, 16.7 eV) have now been constructed utilizing the same simple enclosed-lamp design as described before[2] for argon, krypton, and xenon lamps. Aluminum, which transmits in this wavelength region, was considered to be the best material for a window.[6a] The window was thus constructed of an aluminum[6b] film, 2000–4000 Å thick, attached to a fine-mesh backing. These titanium gettered lamps only emit the strongly reversed rare gas resonance lines. They are leak-free and capable of withstanding a pressure differential of at least 25 torr without damage to the window. The helium lamp used in this study actually has been operated for 1000 hr without deterioration; there is no diffusion of helium through the window. The lamps will be described in detail in a later publication.[7] The intensity of the helium lamp, ~10^{13} quanta/sec, varied by not more than 5% during the course of an experiment, or from one experiment to another.

Initial results on the photolysis of methane at 584 Å are summarized here. Methane (IP = 12.5–12.7 eV)[8,9] was chosen for this preliminary study because considerable information is available about the photoionization of this compound in this wavelength region.[9–11] In addition, the ionization of methane by collision with excited helium atoms[12,13] and the photolysis of methane with the helium resonance line in a windowless apparatus[14] have been investigated.

In the experiments reported here, the lamp was sealed into a reaction vessel fitted with parallel plate electrodes so that saturation ion currents could be measured during the course of an experiment. A comparison of the saturation current measured in methane with that measured in xenon under identical conditions leads to the information that the ionization quantum yield of methane is 0.95 ± 0.05 (assuming that the value for xenon is unity). (A value of 0.75 for the ionization quantum yield of methane at this wavelength has been reported in the literature.[8]) It follows that, when methane is irradiated with the helium resonance line, about 95% of the photons absorbed lead to ionization

$$CH_4 + h\nu\ (21.2\ \text{eV}) \longrightarrow [CH_4^+]^* + e \qquad (1)$$

It should be mentioned that the electrons released in process 1 have a maximum of 8.5 eV energy, and therefore electronic excitation in methane by these electrons can be ignored. This was confirmed by the observation that addition of helium as a moderator did not have any noticeable effect on the product yields.

The methane parent ions may dissociate

$$[CH_4^+]^* \longrightarrow CH_3^+ + H \qquad AP = 14.3\ \text{eV} \qquad (2)$$

$$[CH_4^+]^* \longrightarrow CH_2^+ + H_2 \qquad AP = 15.2\ \text{eV} \qquad (3)$$

or react with neutral methane molecules

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (4)$$

In this study, the CH_4^+ and CH_3^+ ions were determined by neutral product analysis in experiments utilizing the ion interceptor technique employed previously in the radiolysis.[15] The methane was photolyzed in the presence of about 5% added isobutane-d_{10}, and NO was added as a free-radical scavenger. In this system, the following reactions will occur.

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad (5)$$

$$C_2H_5^+ + i\text{-}C_4D_{10} \longrightarrow \underline{C_2H_5D} + C_4D_9^+ \qquad (6)$$

The CH_5^+ ions formed in reaction 4 will transfer a proton to i-C_4D_{10}, leading to the formation of C_3D_8 and CD_3H as products.

$$CH_5^+ + i\text{-}C_4D_{10} \longrightarrow CH_4 + C_4D_{10}H^+ \longrightarrow CH_4 + \underline{CD_3H} + C_3H_7^+ \qquad (7)$$

$$C_3D_7^+ + i\text{-}C_4D_{10} \longrightarrow \underline{C_3D_8} + C_4D_9^+ \qquad (8)$$

(The underscored products in eq 6–8 are those whose yields are determined.)

---

(1) This research was supported in part by the Atomic Energy Commission.

(2) P. Ausloos and S. G. Lias, *Radiat. Res. Rev.*, **1**, 79 (1968).

(3) (a) S. G. Lias and P. Ausloos, *J. Chem. Phys.*, **48**, 392 (1968); (b) R. D. Doepker, S. G. Lias, and P. Ausloos, **46**, 4340 (1967).

(4) S. Lias and P. Ausloos, *Ber. Bunsenges. Phys. Chem.*, **72**, 187 (1968).

(5) P. Ausloos and S. G. Lias, *J. Chem. Phys.*, **45**, 524 (1966).

(6) (a) W. R. Hunter, D. W. Angel, and T. Tousey, *Appl. Opt.*, **4**, 891 (1965). (b) The window was fabricated using the process developed by P. Werner and M. Narasimham, described in National Bureau of Standards, Technical News Bulletin, U. S. Government Printing Office, Dec 1967, p 262.

(7) P. Ausloos and R. E. Rebbert, submitted for publication.

(8) P. H. Metzger and G. R. Cook, *J. Chem. Phys.*, **41**, 642 (1964).

(9) W. A. Chupka, *ibid.*, **48**, 2337 (1968).

(10) B. Brehm, *Z. Naturforsch.*, **21a**, 196 (1966).

(11) V. H. Dibeler, M. Krauss, R. M. Reese, and F. N. Harllee, *J. Chem. Phys.*, **42**, 3791 (1965).

(12) V. Cermak and Z. Herman, *Collection Czech. Chem. Commun.*, **30**, 170 (1965).

(13) J. A. Herce, J. R. Penton, R. J. Cross, and E. E. Muschlitz, Jr., *J. Chem. Phys.*, **49**, 958 (1968).

(14) D. C. Walker and R. A. Back, *ibid.*, **38**, 1526 (1963); R. A. Back and D. C. Walker, *ibid.*, **37**, 2348 (1962).

(15) P. Ausloos, S. G. Lias, and R. Gorden, Jr., *ibid.*, **39**, 3341 (1963).