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]

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

## The Photolysis of Methane at 584 Å[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, $\sim 10^{13}$ 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

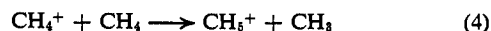$$CH_4 + h\nu \ (21.2 \ eV) \longrightarrow [CH_4^+]^* + e \tag{1}$$
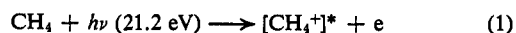
It should be mentioned that the electrons released in process 1 have a maximum of 8.5 eV energy, and therefore electronic excitation in methane by these electrons can be ignored. This was confirmed by the observation that addition of helium as a moderator did not have any noticeable effect on the product yields.
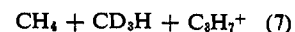
The methane parent ions may dissociate

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

$$[CH_4^+]^* \longrightarrow CH_2^+ + H_2 \qquad AP = 15.2 \ eV \tag{3}$$
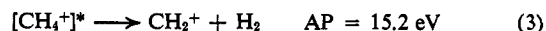
or react with neutral methane molecules

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \tag{4}$$

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.

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \tag{5}$$

$$C_2H_5^+ + i\text{-}C_4D_{10} \longrightarrow \underline{C_2H_5D} + C_4D_9^+ \tag{6}$$
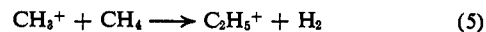
The CH_5^+ ions formed in reaction 4 will transfer a proton to i-C_4D_{10}, leading to the formation of C_3D_8 and CD_3H as products.

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

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

(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).

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(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.

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(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).

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(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).

Accepting that in such a system the yields of C_2H_5D and CD_3H are equivalent to the yields of the $CH_3{}^+$ and $CH_4{}^+$ ions, respectively,[15] we can derive a value of 0.85 for the ratio $CH_4{}^+/CH_3{}^+$, independent of pressure from 1 to 5 torr. Considering the differences in experimental techniques, this value is in fair agreement with the value of 1.1 obtained by Dibeler, et al.,[11] and to the values of 0.67 and 0.95 measured for the $CH_4{}^+/CH_3{}^+$ ratio in methane ionized by collision with excited metastable (2 $^1S_0$ and 2 $^3S_1$) helium atoms (20.6 and 19.8 eV, respectively) in the study of Herce, et al.[13] In the latter study, and in the present one, the methane ion/methyl ion ratio did not change when CD_4 was substituted for CH_4.

The total ion pair yield of $CH_4{}^+$ plus $CH_3{}^+$, derived from product yields and saturation current measurements, was 0.86. As will be discussed later,[7] possibly 5–10% of the $[CH_4{}^+]^*$ ions undergo process 3 to form $CH_2{}^+$.

We also examined the rare gas sensitized photolysis of methane, in which methane ions with varying amounts of excess energy can be formed by charge transfer from different rare gas ions. As anticipated,[16] at constant intensity and at pressures where all quanta are absorbed, the saturation current values measured for pure xenon, krypton, and argon were identical. In contrast, a current of only about 3% of that value was seen when neon (IP = 21.56 eV) was introduced into the vessel.

In experiments where the rare gas/methane ratio was about 10, and the total pressure 15 torr, methane ions are formed mainly by charge transfer

$$A + h\nu \ (21.2 \text{ eV}) \longrightarrow A^+ + e \tag{9}$$

$$A^+ + CH_4 \longrightarrow [CH_4{}^+]^* + A \tag{10}$$
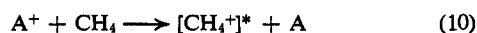
The $CH_4{}^+/CH_3{}^+$ ratios, determined by the interceptor technique described above, are given in Table I for the

Table I. Rare Gas Sensitized Photolysis of Methane

	Kr^+ 14.00–14.66 eV	Ar^+ 15.76–15.93 eV
$CH_4{}^+/CH_3{}^+$	1.25	<0.07
	1.60[a]	0.01[a]

[a] Data of H. von Koch, *Arkiv Fysik*, **28**, 529 (1965).

krypton- and argon-sensitized photolyses. The results agree reasonably well with those of von Koch,[17] measured in a tandem mass spectrometer at a pressure of approximately 10^{-5} torr.

In all the rare gas sensitized photolyses, the ion pair yields which could be attributed to the hydrocarbon ions were close to unity, indicating that charge-transfer process 10 is efficient.

A more detailed account of the far-ultraviolet photolysis of CH_4 and other hydrocarbons carried out with an enclosed neon resonance lamp, as well as the helium resonance lamp, is forthcoming. The ion-

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(17) H. von Koch, *Arkiv Fysik*, **28**, 529 (1965); see also: F. H. Field, H. N. Head, and J. L. Franklin, *J. Am. Chem. Soc.*, **84**, 1118 (1962); G. G. Meisels, W. H. Hamill, and R. R. Williams, Jr., *J. Phys. Chem.*, **61**, 1456 (1957).

ization quantum yields of a variety of organic and inorganic compounds will also be reported shortly.[18]

R. E. Rebbert, P. Ausloos
National Bureau of Standards
Washington, D. C. 20234

Organic Esters of Xenon

Sir:

Upon adding a few crystals of XeF_2 to excess trifluoroacetic acid, solid silver trifluoroacetate, and solid sodium acetate, we have obtained products whose mass spectra show the presence of nonvolatile xenon and fail to show the presence of xenon fluorides. We interpret these results as indirect evidence in favor of the formation of xenon ditrifluoroacetate and xenon diacetate according to the simple scheme

$$XeF_2 + 2RCOOH \longrightarrow Xe(OCOR)_2 + 2HF \qquad R = CF_3$$

and

$$XeF_2 + 2RCOOM \longrightarrow Xe(OCOR)_2 + 2MF \qquad R = CF_3, CH_3$$

although such an interpretation must, in the absence of further information, be considered speculative. As a study of the hypothesized xenon esters and the many xenon compounds related to them would require a serious experimental program which we are not prepared to undertake at present, we have decided to report these results, preliminary and incomplete though they be.

The possibility of synthesizing organic compounds containing xenon using rather typical procedures of organic chemistry has been discussed by the author[1] and independently by Hellwinkel[2] as part of discussions of higher valence compounds of elements in groups V–VIII of the periodic table. The experiments described here were undertaken in order to illustrate the theoretical contention[1] that xenon should have a chemistry similar to that of iodine, which, in turn has a chemistry similar to that of selenium, tellurium, phosphorus, and arsenic.[3] In the only previous study on organic xenon compounds, and which seems not to have been followed up elsewhere in the literature, Iskraut, Taubenest, and Schumacher[4] have prepared what are perhaps $Xe(OCOCF_3)_4$ and $Xe(OCOCH_3)_4$.

(1) (a) J. I. Musher, "The Chemistry of Hypervalent Molecules," *Angew. Chem.*, in press; *Science*, **141**, 736 (1963). For related syntheses, see (b) W. C. Agosta, *Tetrahedron Letters*, 2681 (1965), and (c) H. K. Livingston, J. W. Sullivan, and J. I. Musher, *J. Polymer Sci.*, **C22**, 195 (1968). Xenon diacetate is discussed along with other related compounds in (d) J. I. Musher, "Higher Valences, Geometrical Isomers and New Molecules," 1964, (privately circulated); (e) "Higher Valence Inorganic Cyclic Diesters," 1965, unpublished.
(2) D. Hellwinkel, lecture on the 70th birthday of G. Wittig, 1968, unpublished.
(3) See, e.g., D. Hellwinkel and G. Fahrbach, *Chem. Ber.*, **101**, 574 (1968), and previous articles cited therein.
(4) A. Iskraut, R. Taubenest, and E. Schumacher, *Chimia*, **18**, 188 (1964).