observation by Hachisu *et al.* (*5*). In simple ionic systems, the presence of void structures can be inferred at least qualitatively from extended x-ray absorption fine structure data, which showed that the average distance between Zn^{2+} and Br^- is 2.37 Å in 0.089 M $ZnBr_2$ aqueous solutions and 2.30 Å in 0.05 M solutions (*12*). These values are very close to the interionic distance observed in the crystalline state (2.40 Å). From these findings, it was claimed that "some local order, resembling that of the corresponding crystals, exists" in the aqueous solutions. The same conclusion was also reached for $NiBr_2$-ethyl acetate solutions (*13*) and aqueous $CuBr_2$ solutions (*14*). Comparing the reported interionic distances with the average interionic distance (22 and 19 Å for 0.05 and 0.089 M solutions, respectively) $[\approx(1000/3CN_A)^{1/3}$, where C is the molar concentration and N_A is Avogadro's number], we estimate that local order occupies only a very small portion of the solution volume, implying that voids occupy most of the solution volume. It should be mentioned that local structures and also voids in simple ionic solutions, such as metal halides, have very short life-spans (*15*).

The following recent finding suggests that microscopic inhomogeneity in solute distribution is a general characteristic of ionic systems. Matsumoto *et al.* (*16, 17*) studied single Langmuir-Blodgett (LB) films of fatty acids and their barium salts by dark-field electron microscopy and found the coexistence of solid, liquid, and gas structures (being "hole" or "porous," according to their terminology). Amazingly, pictures of holes as large as 4 μm in diameter can be seen in the film [figure 9 of (*17*) for arachidic acid]: It does not seem unreasonable to imagine much larger holes in the solutions before they are cast into film. Atomic force microscopy (AFM) has revealed domain formation in "liquid-like" regions in LB films (*18*). Although it is not clear from the AFM images whether void structures were maintained in the space between the domains, this study clearly demonstrates structural inhomogeneities that could not be seen by conventional fluorescence microscopy.

Needless to say, relatively rapid Brownian agitation of small ionic species smears out the void structures so that their presence does not matter on the time scale of thermodynamic measurements. On the other hand, the long time scale of the motion of latex particles and their size enabled us to make real time microscopic observations of structural inhomogeneities, such as two-state structure and void formation in colloidal dispersions. Such structural inhomogeneities would seem to be important if the thermodynamic properties of the dispersions are to be thoroughly understood.

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15. A crude estimate of the volume of the local order would be 1/1000 $[\approx(2.30/22)^3]$ and 2/1000 $[\approx(2.37/19)^3]$ of the total solution volume at 0.05 and 0.089 M, respectively. This implies that the void volumes are 999/1000 and 998/1000, respectively. Naturally, this is based on the assumption that all ionic species exist in the local order, which is of course extreme because some (unknown) portion of ionic species exist as free ions. Thus, the above calculation overestimates the void volume.
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Synthesis and Characterization of Molybdenum Carbide Clusters Mo_nC_{4n} (n = 1 to 4)

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Laser radiation (XeCl laser, 308-nanometer wavelength) focused into a cell containing $Mo(CO)_6$ vapor produced ultrafine particles in the extended waist of the laser beam. Negative ion mass spectrometry revealed molybdenum carbide cluster ions with a stoichiometry Mo_nC_{4n} (n = 1 to 4). The $Mo_nC_{4n}^-$ (n = 2 to 4) ions are completely unreactive with NH_3, H_2O, and O_2, suggesting structures in which the molybdenum atoms are unavailable for coordination to additional ligands. Collision-induced dissociation studies of these anions show the loss of MoC_4 units as the main fragmentation pathway. This observation, together with the lack of addition reactions, provides a basis for structures in which a planar cluster of two, three, or four molybdenum atoms is surrounded by, and bonded to, carbon dimers.

Mechanisms leading to the multiphoton excitation and ionization of organometallic molecules are of considerable current interest. Multiphoton excitation of many organometallic compounds in the gas phase leads to the copious formation of bare metal atoms and metal ions (*1*). Laser irradiation of organometallic vapors has found many applications in chemical vapor deposition (*2*).

Recent studies (*3, 4*) have reported the formation of ultrafine particles when gas-phase carbonyls of transition metals such as $Mo(CO)_6$, $Cr(CO)_6$, and $W(CO)_6$ were exposed to XeCl laser radiation. Scanning electron microscopy studies indicated that the particles are less than 1 μm in diameter. The composition and properties of these particles were not characterized. In this report, we present a detailed description of the identification and characterization of the bulk material formed by XeCl laser irradiation of $Mo(CO)_6$ in the gas phase. A class of molybdenum carbide clusters, Mo_nC_{4n} (n = 1 to 4), was observed. The stoichiometry and properties of these clusters were examined by laser desorption Fourier transform ion cyclotron resonance mass spectrometry (FTMS) and thermal desorption electron capture mass spectrometry. FTMS ion-trapping and manipulation techniques were also used to examine the collision-induced dissociation, ion-molecule reactions, and charge exchange reactions of

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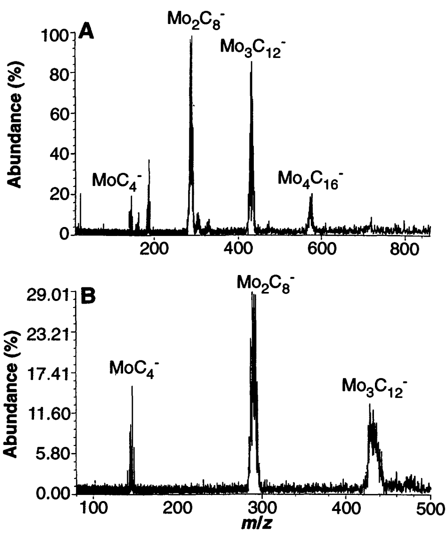

Fig. 1. (**A**) Negative ion Fourier transform mass spectrum obtained by laser desorption of particles generated by photolysis of $Mo(CO)_6$. (**B**) The CID of $Mo_3C_{12}^-$, revealing fragment ions corresponding to $Mo_2C_8^-$ and MoC_4^-.

these new species to study their fragmentation pathways, reactivities, and electron affinities (EAs). The structures and properties of these molybdenum carbide clusters are compared with the recently proposed cage-structured metallo-carbohedrenes (met-cars) (*5–8*).

The laser photolysis of $Mo(CO)_6$ was performed in a stainless steel chamber (35 cm by 35 cm by 12 cm) equipped with entrance and exit quartz windows. The chamber was initially evacuated to 10^{-6} torr and then filled with $Mo(CO)_6$ to a pressure of 0.1 torr. A XeCl laser beam [308 nm, 30 mJ/pulse, 15-ns pulse width (full width at half maximum)] was focused by a quartz lens with a focal length of 20 cm, giving a focal spot of 0.1 cm by 0.2 cm in the stainless steel chamber. The fluence at the focal spot was estimated to be 1.5 J/cm^2 (power density = 10^8 W/cm^2).

The ultrafine particles formed by this technique slowly settled to the bottom of the chamber and were collected on a glass substrate located a few centimeters below the laser beam axis. The repetition rate of the laser was 2 Hz, and the irradiation time was 6 hours. The ultrafine particles remained in the pulsed laser field for ~1 s (two pulses) (*3*). During the irradiation, the metal carbonyl vapor in the chamber was pumped out and refilled every 15 min.

The presence of ultrafine particles in certain regions of the ultraviolet laser beam was monitored by HeNe laser light scattering. The spatial probing by the HeNe laser beam propagating coaxially with the XeCl laser beam showed that the regions of formation of ultrafine particles were localized near but not included within the focal point of the lens, in the fluence range of 0.1 to 0.4 J/cm^2 (*3*). There was no scattered light observed in the central focal region of the lens, suggesting the absence of particles large enough to scatter the light and presumably the presence of particles of atomic dimension.

The positive ions generated by laser-desorption FTMS (9) of the ultrafine particles collected from the laser photolysis of $Mo(CO)_6$ consisted primarily of atomic Mo cations, with a small amount of molybdenum carbide clusters $Mo_2C_x^+$ ($x = 0$ to 8) and $Mo_3C_z^+$ ($z = 0$ to 12). In contrast, the negative ion laser desorption FTMS spectra revealed several abundant ions consisting of molybdenum carbide clusters of the stoichiometry $Mo_nC_{4n}^-$, where $n = 1$ to 4 (Fig. 1A). High-resolution mass spectrometry was used to determine the empirical formulas of these ions and the number of Mo atoms per cluster (obtained by examination of the isotopic abundances of Mo). Abundant ions corresponding to MoC_4^-, $Mo_2C_8^-$, $Mo_3C_{12}^-$, and $Mo_4C_{16}^-$ were observed. No $Mo_8C_{12}^-$ (mass-charge ratio $m/z = 912$) was observed. Although laser-induced fragmentation of the larger clusters may be responsible for some of the smaller clusters, variation of laser pulse energies did not significantly alter the intensity distribution of the mass spectra. This suggests that the particles consist of a mixture of Mo carbides and not of exclusively Mo_4C_{16}. In fact, a small signal was often observed at $Mo_5C_{20}^-$, indicating the presence of larger clusters as well.

Even though low laser power densities were used for the experiments outlined above, it is possible that the laser desorption event altered the sample by creating species that were not originally present. To see if this was the case, we examined the thermal desorption mass spectrometry. For this process, a solid sample of the ultrafine particles was heated inside the mass spectrometer to desorb the sample, which was then ionized by electron capture ionization. Thermal desorption (400°C, the maximum allowed) electron capture FTMS of the sample did not yield any ions, indicating that this temperature was not sufficient to desorb the sample. Higher temperature thermal desorption was successful on a magnetic sector instrument (*10*). A small amount of the sample was loaded onto a coiled platinum or rhenium wire, which was then resistively heated to temperatures up to ~1800°C in the ion source of the mass spectrometer operating under electron capture conditions. This technique revealed a strong signal corresponding to $Mo_2C_8^-$ and $Mo_3C_{12}^-$ and a weaker signal at MoC_4^-, as well as less abundant cluster ions in the region where $m/z = 200$ to 400. This clearly demonstrates that the appearance of these same ions in the FTMS was not merely an artifact of the laser desorption and ionization. Thermal desorption mass spectrometry of commercial Mo_2C was also attempted. Negative ions were not observed, implying that either this material does not thermally desorb, or it does not form stable negative ions. The disparate results obtained under similar conditions for the two samples indicate that the samples are quite different.

Glow discharge mass spectrometry (GDMS) (*11*) was used to examine the elemental composition of the ultrafine particles. Careful inspection of the mass spectra revealed that the atomization process was quite efficient (molecular species such as MoC^+, $Mo_2C_8^+$, and others were not observed above the detection limit of 1 part per billion). With use of Mo_2C as a reference material for calibration, GDMS of the ultrafine particles from the laser photolysis of $Mo(CO)_6$ yielded the following average weight percentages: 51.8% C, 46.1% Mo, 1.6% Fe, 0.29% O, and 0.22% Ni. Molar stoichiometries in the range of MoC_5 to MoC_7 were obtained from inspection of multiple samples, the mean of which is the exact Mo/C ratio for $Mo(CO)_6$. On first sight, this appears to contradict the stoichiometry expected from the mass spectra in Fig. 1A; however, GDMS examines the bulk material and does not provide information about the molecular nature of the particles. This sample is undoubtedly a mixture of products and is not exclusively $(MoC_4)_n$. Two factors about the GDMS results must be clarified: (i) quantification of the light elements (C, O) is more uncertain than that of the metals because of large differences in sensitivity, and (ii) the presence of a small amount of graphitic carbon in the sample is likely; this would make the measured ratio of Mo/C too low. Only a trace of oxygen is present in the sample (0.29%), showing that carbon is not mainly present as adsorbed CO or CO_2. The presence of a small amount of iron (1.6%) is somewhat surprising. The GDMS results verify that the sample consists primarily of Mo and C, which are present in a dramatically different molar ratio than that observed for Mo_2C.

Collision-induced dissociation (CID) experiments for each of the clusters were performed with the FTMS to investigate the fragmentation pathways (*12*). The CID of $Mo_2C_8^-$ with argon produced only MoC_4^-. No loss of Mo, MoC_2, C_2, or C_2^- was observed. Collision of $Mo_3C_{12}^-$ with argon produced $Mo_2C_8^-$ exclusively, which further fragmented to produce MoC_4^-, (Fig. 1B). Once again, no other fragment ions were observed. Electron detachment was not readily observed at these collision energies, suggesting that either the cross section for dissociation is much larger than that for electron detachment at these energies or that these species have EAs that exceed the bond dissociation energies, that is, EA(Mo_nC_{4n}) > $D_0(MoC_4^- \text{-} MoC_4)$. $Mo_4C_{16}^-$ undergoes dissociation to give primarily $Mo_2C_8^-$ and presumably Mo_2C_8 (symmetric fission). We did not observe $Mo_3C_{12}^-$ or MoC_4^- as fragmentation products for this ion.

To examine the reactivity of these molybdenum carbides ($Mo_nC_{4n}^-$, $n = 2$ to 4), we examined a series of ion molecule reactions. In particular, the $Mo_nC_{4n}^-$ cluster anions were trapped in the FTMS cell for 2 s in the presence of O_2, CO_2, H_2O, or NH_3 at a static pressure of $\sim 1 \times 10^{-6}$ torr. No reactions were observed in any of these cases. The absence of these reactions imply structures for the $(MoC_4)_n^-$ clusters in which the Mo atoms are not accessible to these small reactive gases.

Charge exchange reactions of the $Mo_nC_{4n}^-$ ions with other reagent gases were used to "bracket" the adiabatic EAs of Mo_nC_{4n}. As an example, we monitored reaction 1 to examine possible charge exchange between $Mo_2C_8^-$, $Mo_3C_{12}^-$, and chloranil, $C_6O_2Cl_4$ [EA = 2.7 ± 0.2 eV (*13*)] (Fig. 2A)

$$Mo_nC_{4n}^- + C_6O_2Cl_4 \rightarrow Mo_nC_{4n} + C_6O_2Cl_4^- \qquad (1)$$

where $n = 2$ or 3.

This reaction does not occur (no chloranil anions are observed), implying that the EAs of both Mo_2C_8 and Mo_3C_{12} are greater than 2.7 eV. However, at long interaction time, an association product is observed for reaction 1 (Fig. 2B). The $(Mo_2C_8 + \text{chloranil})^-$ ion was isolated (Fig. 2C) and collisionally dissociated. The only ionic product observed was $Mo_2C_8^-$ (Fig. 2D), again implying that EA(Mo_2C_8) > EA(chloranil) = 2.7 ± 0.2 eV. Similar experiments indicated that EA(Mo_3C_{12}) > EA(chloranil). Preliminary experiments have indicated that both $Mo_2C_8^-$ and $Mo_3C_{12}^-$ charge exchange with tetracyanoquinodimethane (TCNQ) [EA = 3.3 ± 0.3 eV (*14*)]. These results bracket the electron affinity of Mo_2C_8 and Mo_3C_{12} between 2.7 and 3.3 eV. Unfortunately, the small abundance of MoC_4^- and $Mo_4C_{16}^-$ in the mass spectra prohibited similar investigations of the charge exchange reactions of these species.

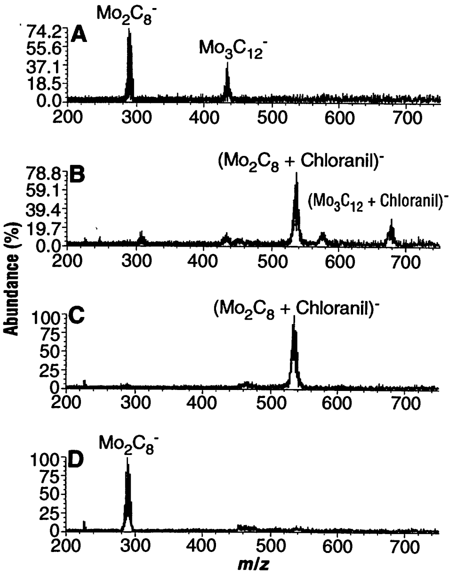

Fig. 2. Charge exchange reaction of the $Mo_nC_{4n}^-$ (n = 2 or 3) ions with chloranil ($C_6O_2Cl_4$). Negative ion mass spectra (**A**) before and (**B**) after reaction. Isolated $(Mo_2C_8 + C_6O_2Cl_4)^-$ ion (**C**) before and (**D**) after CID.

One interesting feature of the molybdenum carbide material is the presence of a small fraction of ferromagnetic particles in the photolysis product. A bar magnet was used to identify and separate the ferromagnetic material, which also had the appearance of black particles. Microprobe x-ray fluorescence measurements revealed the presence of iron in these particles. The elemental analysis outlined above also showed that iron is present in these samples. This was confirmed by magnetic susceptibility measurements, which showed that the ferromagnetism could be completely explained by the presence of iron in the sample. The negative ion mass spectra show that iron is not present in the molybdenum carbide clusters (Fig. 1A) but rather may be present as elemental iron or iron oxide. Of course, it may not be possible to inject strongly ferromagnetic clusters into a FTMS because of the strong (3-T) magnetic field. The origin of the iron in the sample is quite intriguing because this solid sample is generated by laser photolysis of gas-phase $Mo(CO)_6$. One possibility is that iron is leached out of the stainless steel chamber (perhaps by ambient CO).

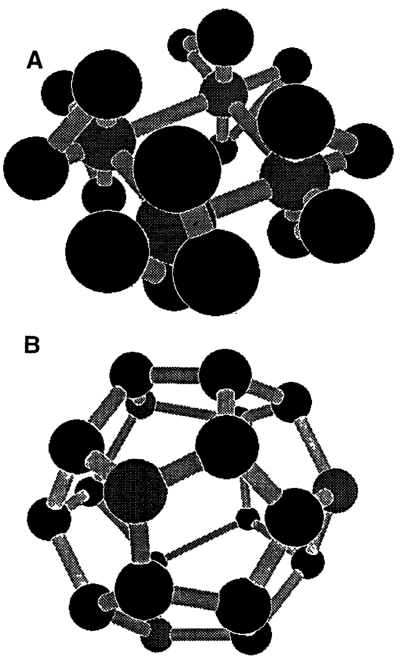

Fig. 3. Possible structures of Mo_4C_{16} (darker shade corresponds to carbon). (**A**) Structure resulting from the assembly of MoC_4 subunits where the molybdenum atoms are joined. In this structure, the molybdenum atoms are protected from reaction by the surrounding acetylenic C_2 groups. (**B**) Alternative dodecahedral structure similar to the originally proposed metallocarbohedrene structure.

The experimental results outlined above provide information about the possible structures of these metal carbides. One possible structure for $Mo_4C_{16}^-$ (Fig. 3A) consists of four MoC_4 subunits that are bound together by four Mo-Mo bonds. The symmetric arrangement allows the C_2 units to be placed equally distant from one another. This type of bicoordinate C_2 ligand has previously been identified in the compounds BC_2 (*15*) and AlC_2 (*16*) in cryogenic matrices resulting from the laser ablation of boron carbide and aluminum carbide. Symmetric cleavage of two Mo-Mo bonds would result in the formation of neutral Mo_2C_8 fragments or $Mo_2C_8^-$ fragments, which supports the CID spectra. The Mo atoms in $Mo_4C_{16}^-$ for this structure should be quite unreactive with respect to the addition of Lewis bases such as ammonia or water. Similar structures can be drawn for $Mo_3C_{12}^-$ and $Mo_2C_8^-$ as well.

Recently, other metallo-carbohedrenes of stoichiometry A_8C_{12} have been synthesized for A = Zr, Hf, Ti, and V (*5–8*). Initially, these species were proposed to exist as spherical cage structures, termed met-cars, in which all of the atoms are present on the surface of a dodecahedron, similar to the smallest possible fullerene, C_{20}. Castleman and co-workers (*6*) have used the observation that NH_3 readily attaches to the clusters (V_8C_{12} and Ti_8C_{12}) to infer their dodecahedral caged (met-car) structure. This proposed structure has been supported by the calculations of Reddy *et al.* (*7*). More recent calculations support a distorted dodecahedron (*17–20*). Although $Mo_4C_{16}^-$ is also a 20-atom molecule for which a met-car–like dodecahedral (Fig. 3B) or distorted dodecahedral structure could be proposed, this structure is not consistent with the lack of reactivity of $Mo_4C_{16}^-$ with ammonia. In addition, these Mo_nC_{4n} clusters dissociate exclusively by sequential MoC_4 losses, in contrast to the M_8C_{12} met-car compounds, which fragment by M or MC_2 loss (*21*). The data for Mo_nC_{4n} favor an alternative structure, perhaps similar to the one shown in Fig. 3A.

In conclusion, laser photolysis of gas-phase metal carbonyls is a useful method for the bulk synthesis of metal carbides having possibly unique structures and properties. The Mo_nC_{4n} clusters reported here are clearly not of the same general structure of the met-car class. Pilgrim and Duncan (*22*) have recently reported $Mo_8C_{12}^+$ ionic clusters presumably of the met-car class. Molybdenum carbide generally has the stoichiometry MoC or Mo_2C. Both of these carbides have long been known to be superconductive alloys with critical temperatures $T_c = 12.2$ K for Mo_2C and $T_c = 6.5$ and 9.26 K for MoC. Conductivity measurements of the Mo_nC_{4n} films produced in this study are currently under way. Efforts have begun to first purify and to further investigate the physical properties of the clusters reported here.

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9. An Extrel (Madison, WI) FTMS-2000 Fourier transform mass spectrometer equipped with a Spectra-Physics DCR-11 pulsed yttrium-aluminum-garnet–Nd (YAG-Nd) laser (355 nm, 8-ns pulse width). For the FTMS experiments, the YAG-Nd laser was focused to a spot ~300 μm in diameter (10^6 to 10^7 W/cm^2) to desorb and simultaneously ionize the sample on the stainless steel disk. Although the power density of the laser radiation used to desorb and ionize the sample was kept low, it is possible that this desorption-ionization event produced some dissociation of the analyzed material. The resulting ions were then trapped and detected in the FTMS ion cell. Both positive and negative ions were examined in the region m/z = 20 to 4000. For most experiments, the ions were produced in the laser desorption event at a background pressure of 8×10^{-8} torr and then trapped for 3 to 20 ms before detection.
10. Mass spectra were obtained in this case with a VG-Analytical ZAB-EQ double-focusing magnetic sector–quadrupole hybrid instrument. Thermal desorption was accomplished by the resistive heating of a coiled Pt or Re wire.
11. Glow discharge mass spectra (positive ions) were obtained with a VG-9000 magnetic sector instrument. The glow discharge was established in an ionization region maintained with 1 torr of argon. Solid samples (<1 mg) were pressed onto indium pins. The discharge was established at 1000 V and ~1 mA of direct current. The glow discharge atomizes and ionizes the sample, and the resulting positive ions are extracted from the source region and separated by a magnetic sector before detection. The efficiency of the atomization and ionization processes are dependent on the elements to be examined and the physical nature of the sample. Best results are obtained when similar samples are used to provide calibration factors for the elements to be determined.
12. To perform the CID experiments, we isolated a selected parent ion in the FTMS cell and then accelerated that ion up to a center-of-mass collision energy of 5 to 20 eV in the presence of a static pressure of argon at 4×10^{-6} torr. Collisions between the molecular ion and the background argon gas resulted in the fragmentation of the accelerated ions. Multiple collisions of the excited ion with argon may have occurred before dissociation, especially at the low collision energies.
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22. R.E.H. acknowledges support by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge Institute for Science and Education and the Oak Ridge National Laboratory. We are indebted to B. Sales for providing the x-ray fluorescence and magnetic susceptibility measurements reported herein. Research sponsored by the Directors Research and Development Fund, the Office of Health and Environmental Research, and the Office of Basic Energy Sciences, Oak Ridge National Laboratory, U.S. Department of Energy (DOE), under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. A.V.D., A.A.P., and the research at the Institute of Spectroscopy were supported, in part, by DOE. The University of Tennessee, Knoxville, Mass Spectrometry Center is supported by The Science Alliance, a State of Tennessee Center of Excellence.

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Do Hydrofluorocarbons Destroy Stratospheric Ozone?

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Hydrofluorocarbons, many of which contain a CF_3 group, are one of the major substitutes for the chlorofluorocarbons and halons that are being phased out because they contribute to stratospheric ozone depletion. It is critical to ensure that CF_3 groups do not cause significant ozone depletion. The rate coefficients for the key reactions that determine the efficiency of the CF_3 radical as a catalyst for ozone loss in the stratosphere have been measured and used in a model to calculate the possible depletion of ozone. From these results, it is concluded that the ozone depletion potentials related to the presence of the CF_3 group in hydrofluorocarbons are negligibly small.

The global phase-out of the ozone-damaging chlorofluorocarbons (CFCs) and halons (chlorofluorobromocarbons) has led to various proposed substitutes. Many of the substitute compounds are hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). The short lifetimes of the HCFCs make them much less damaging to the ozone layer than the CFCs. The HFCs contain no chlorine or bromine, only fluorine. In contrast to chlorine and bromine, fluorine has been known to be benign toward the ozone layer. The HFCs have therefore been assumed to have ozone depletion potentials (ODPs) of essentially zero (*1*). (ODP is an index of the ozone depletion ability of a compound relative to CFC-11.) Under the U.S. Clean Air Act Amendments, only compounds with an ODP less than 0.2 may be used as halocarbon substitutes. The major HFCs under consideration or production are CF_3CFH_2 (134a), CF_3CF_2H (125), CHF_3 (23), CF_3CH_3 (143a), and CF_2HCH_3 (152a). In particular, HCFC-134a has begun to be widely used as a substitute for CFCs in air conditioning and refrigeration applications. Many of these HFCs contain a CF_3 functional group.

It has been recently suggested that molecules containing the CF_3 group may represent a special case of fluorine-catalyzed ozone loss (*2*). The CF_3 group is unusually stable and may destroy significant amounts of ozone through catalytic cycles involving CF_3O_x (CF_3O and CF_3OO) radicals (*2*). If this were true, many HFCs (and possibly a few currently acceptable HCFCs) could have ODPs greater than 0.2, and new substitutes would have to be developed. The consequences of such a radical change in scientific understanding for industry, international agreements, and the phase-out

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