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Generation of $F_2C{=}C{=}O$ and $F_2C{=}C{=}O^{\bullet+}$ from Ionized $CF_2{=}CFOCF_3$. First Experimental Observation of Gas-Phase Neutral Perfluoroketene

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Ionized perfluoromethylvinyl ether, $CF_2{=}CFOCF_3$, dissociates chiefly to generate perfluoroketene ions. These were shown to produce the stable neutral perfluoroketene following electron transfer from xenon in a neutralization−reionization mass spectrometry (NRMS) experiment. The perfluoroketene molecules were metastable in the microsecond time frame with respect to their dissociation $CF_2{=}C{=}O \rightarrow CF_2 + C{\equiv}O$.

Introduction

Until recently, perfluoroketene[1] had not been experimentally identified as a stable species in any phase. However, Kotting et al.[2] has proposed the generation of neutral perfluoroketene $F_2C{=}C{=}O$ from a reaction of perfluorovinylidene $F_2C{=}C{:}$ with carbon dioxide $O{=}C{=}O$, via the elimination of $C{\equiv}O$, in a 1% CO_2 doped Ar matrix at 30 K. The matrix-isolated $F_2C{=}C{=}O$ was characterized utilizing IR difference spectroscopy, isotopic labeling, and density functional theory (DFT) calculations, and the asymmetric FCF stretching and symmetric and asymmetric CCO stretching vibrations have been identified. The DFT calculations[2] also proposed a planar stable structure for perfluoroketene $F_2C{=}C{=}O$ with bond angles and bond lengths similar to that of ketene $H_2C{=}C{=}O$ and possessing a small endothermic barrier to the dissociation into $CF_2 + C{\equiv}O$.

Concurrent with the above observations of Kotting et al.,[2] a recent high-level calculation[3] showed $F_2C{=}C{=}O$ to be a stable species with a heat of formation $\Delta_f H°[CF_2{=}C{=}O] = -(290.4 \pm 13.2)$ kJ mol^{-1} and an exothermic dissociation to $CF_2 + C{\equiv}O$ ($\Delta_f H°[CF_2] = -(203.3 \pm 16.5)$ kJ mol^{-1} [3] and $\Delta_f H°[C{\equiv}O] = -(110.5 \pm 0.4)$ kJ mol^{-1} [4]). In addition, the earlier report by Dailey[5] gave the neutral and radical cation forms closely similar geometries with a dissociation barrier of ∼42 kJ mol^{-1} (i.e., 10 kcal mol^{-1}); this makes vertical neutralization of the ion by neutralization−reionization mass spectrometry (NRMS) an attractive technique[6] for the possible first production of stable gas-phase neutral $CF_2{=}C{=}O$.

Relatively few perfluoro molecules are readily available, but fortunately, two possible precursors for ionized perfluoroketene can be obtained, namely, the C_3F_6O isomers $(CF_3)_2C{=}O$ and $CF_2{=}CFOCF_3$. In the case of their hydrogen analogues, ionized acetone produces predominantly $CH_2{=}C{=}O^{\bullet+}$ ions by loss of CH_4 in its metastable ion mass spectrum, where it competes with CH_3CO^+ for the lowest energy fragmentation process.[7,8] In contrast, metastable vinylmethyl ether ($CH_2{=}CHOCH_3$) ions produce mainly CH_3CO^+ fragments via an isomerization to energy-rich acetone ions.[7] The very low heat of formation[4,9] of CF_4, −934.5 kJ mol^{-1}, promised to make the formation of $CF_2{=}C{=}O^{\bullet+}$ from $(CF_3)_2C{=}O^{\bullet+}$ a likely process, but as described below, this expectation was not realized.

Experimental Section

Perfluoroacetone, $(CF_3)_2C{=}O$ (anhydrous), and perfluoromethylvinyl ether, $CF_2{=}CFOCF_3$, were purchased from Synquest Labs Inc., Alachua, FL, and used as received. The experiments were performed on a reverse geometry (BEE) VG-ZAB 3F mass spectrometer that contains four collision cells. The first pair of collision cells is located in the second field-free region (2FFR) (between B and the first E), and the second pair of collision cells is located in the third field-free region (3FFR) (between the electric sectors). The ions were generated by 70 eV electron impact, and they were accelerated to 8 kV. Kinetic energy release values, $T_{0.5}$, were obtained from the peak widths at half-height and evaluated by established methods.[10] Energy resolution was such that the width at half-height of the main ion beam was less than 5 V. The remaining experiments were conducted at low mass resolution and a source pressure of $\sim 5 \times 10^{-6}$ Torr.

As well as metastable ion (MI) mass spectra, collision-induced dissociation (CID) mass spectra were recorded under essentially single collision conditions (10% mass-selected ion beam reduction) with He and O_2 as collision gases. Neutralization−reionization (NR) mass spectra were recorded using the 2FFR or 3FFR cells appropriately and with Xe as the neutralization target and O_2 for reionization. Mass-selected ion beam transmissions were 90% in the 2FFR and 3FFR experiments. All metastable ion (MI), collision-induced dissociation (CID), and neutralization−reionization (NR) mass spectra were shown to be completely artifact-free (by detuning the magnet while transmitting the ions of interest during the tandem mass spectrometric experiments, whereupon all signals in the spectra also vanished).

Results and Discussion

The normal mass spectrum of both $(CF_3)_2C{=}O^{\bullet+}$ and $CF_2{=}CFOCF_3^{\bullet+}$ each contained molecular ions of about 4% and 20%, respectively. For the ketone ion, the major fragment ions were CF_3^+ (100%), CF_3CO^+ (50%), $CF_3COCF_2^+$ (26%), and $CF_2^{\bullet+}$ (15%). The $C_2F_2O^{\bullet+}$ ion was of similar abundance to the molecular ion. The MI mass spectrum contained only CF_3CO^+ (*m/z* 97) and a very weak $C_2F_2O^{\bullet+}$ (*m/z* 78).

The ether produced a dissimilar mass spectrum: base peaks CF_3^+ (100%), $C_2F_3^+$ (25%), $C_2F_2O^{\bullet+}$ (15%), $CF_2^{\bullet+}$ (10%), CFO^+ (9%), and $C_2F_6^{\bullet+}$ (6%). The MI mass spectrum contained a single broad Gaussian peak for CF_4 loss to produce $C_2F_2O^{\bullet+}$ at *m/z* 78. The kinetic energy release (KER) was $T_{0.5} = 80$ meV; the peak was very insensitive to collision gas, in keeping with a rearrangement preceding fragmentation.

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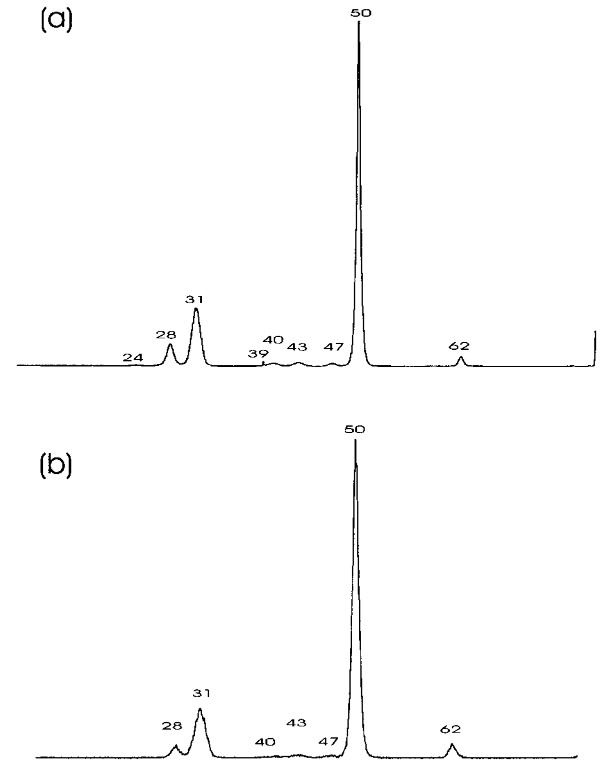

Figure 1. (a) Collision-induced dissociation (CID) 2FFR mass spectrum of source-generated $C_2F_2O^{\bullet+}$ *m/z* 78, He 90% transmittance. (b) Collision-induced dissociation (CID) 3FFR mass spectrum of 2FFR metastably generated $C_2F_2O^{\bullet+}$ (*m/z* 78 from $CF_2{=}CFOCF_3^{\bullet+}$; He 90% transmittance).

Accordingly, the perfluoromethylvinyl ether $CF_2{=}CFOCF_3$ was used in all subsequent experiments.

The MI mass spectrum of $C_2F_2O^{\bullet+}$ ions generated in the ion source from $CF_2{=}CFOCF_3^{\bullet+}$ contained a single Gaussian peak corresponding to $CF_2^{\bullet+}$ (*m/z* 50) with a very small KER, $T_{0.5} = 2.1$ meV, and the peak was collision sensitive, both in keeping with the dissociation being a simple bond cleavage. This observation is remarkably similar to the behavior of ionized metastable ketene $CH_2{=}C{=}O$, where the analogous product ion $CH_2^{\bullet+}$ (*m/z* 14) has a $T_{0.5} = 2.6$ meV.[11]

The CID mass spectrum is shown in Figure 1a together with that for $C_2F_2O^{\bullet+}$ ions generated from metastable $CF_2{=}CFOCF_3^{\bullet+}$ ions, Figure 1b. The major and minor peaks in spectra a and b of Figure 1 are consistent with a single ion structure being generated in the ion source and metastably having the perfluoroketene structure $CF_2{=}C{=}O^{\bullet+}$. Note the doubly charged ion, *m/z* 39 (weak in Figure 1b). The CID mass spectrum of ketene ($CH_2{=}C{=}O^{\bullet+}$) ions also contains a doubly charged ion. The *m/z* 50 peak in the CID mass spectrum of $CF_2{=}C{=}O^{\bullet+}$ is composite, with a very narrow MI signal atop a much broader peak. The KER for the latter is target-gas-independent, $T_{0.5} = 84$ meV.

The NR mass spectrum, Figure 2, is for ion-source-generated $C_2F_2O^{\bullet+}$ ions. It contains a strong recovery signal and the same fragment ions as the CID mass spectra (Figure 1). The peaks in the NR mass spectrum for $CO^{\bullet+}$ and $CF_2^{\bullet+}$ are significantly broader than their CID counterparts and are composite with narrow peaks on very broad, steep-sided bases and are illustrated in Figure 3. The $T_{0.5}$ values for the latter were 550 meV for both fragment ions.

The NR mass spectrum of $C_2F_2O^{\bullet+}$ ions generated metastably in the 2FFR and transmitted to the 3FFR was indistinguishable from that shown in Figure 2. This too is in keeping with only a single ion structure of *m/z* 78 being involved.

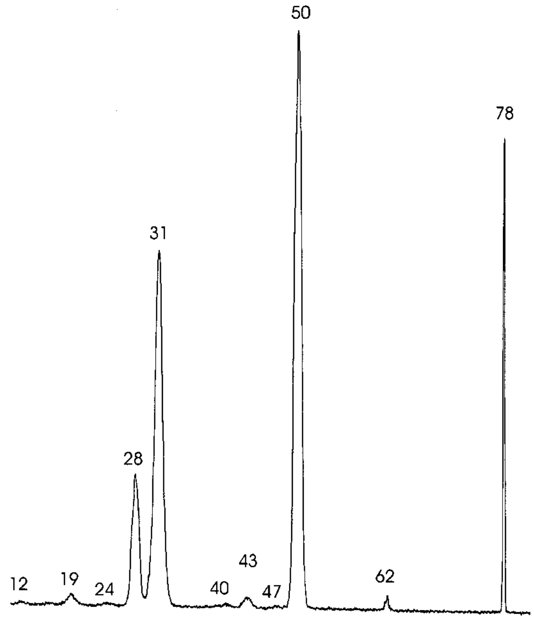

Figure 2. Neutralization−reionization (NR) 2FFR mass spectrum of source-generated $C_2F_2O^{\bullet+}$ (*m/z* 78; Xe, 90% transmittance; O_2, 90% transmittance).

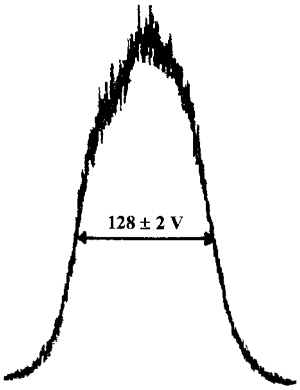

Figure 3. Close-up of the NR mass spectrum signal for $CO^{\bullet+}$ and $CF_2^{\bullet+}$ of source-generated $C_2F_2O^{\bullet+}$ (*m/z* 78, Xe, 90% transmittance; O_2, 90% transmittance).

It is proposed that excited neutral $CF_2{=}C{=}O$ molecules dissociate readily to produce (after collisional ionization) the very broad components of the $CF_2^{\bullet+}$ and $CO^{\bullet+}$ ion peaks. The narrow components are compatible with dissociation of excited reionized stable $CF_2{=}C{=}O$.

All the above experimental observations are incompatible with isomeric C_2F_2O ions or neutrals. The cyclic perfluorooxirene has been predicted by ab initio calculations to be only a saddle point on the potential surface.[12] Perfluoromethynol, $FC{\equiv}COF$, is highly unlikely to be responsible for the above mass spectra.

The results of the experiments allow one to remark upon the energetics of the $CF_2{=}C{=}O$ ion and neutral.

First, the ion was generated as a prominent fragment ion from $CF_2{=}CFOCF_3^{\bullet+}$, the dissociation being accomplished by a significant kinetic energy release, 80 meV. A KER of this magnitude implies the presence of a reverse energy barrier for the reaction, and so the $CF_2{=}C{=}O^{\bullet+}$ ions must have been generated above their thermochemical threshold. Note that an appearance energy (AE) measurement would not have provided useful information regarding the $\Delta_f H°[CF_2{=}C{=}O^{\bullet+}]$. Not only does the $CF_2{=}CFOCF_3^{\bullet+}$ dissociation have a reverse energy

TABLE 1: Summary of the Heat of Formation and Dissociation Product Limits for the Radical Cation Manifold of $F_2C{=}C{=}O$

species	heat of formation, $\Delta_f H°$ (kJ mol^{-1})[a]
$CF_2{=}C{=}O^{\bullet+}$	≤736b
$CF_2^{\bullet+} + C{\equiv}O$	786
$CF^+ + FC{=}O^\bullet$	978
$FC{=}O^+ + CF^\bullet$	1000
$C{\equiv}O^{\bullet+} + CF_2$	1037
$CF^+ + F^\bullet + C{\equiv}O$	1102
$FC{\equiv}CF^{\bullet+} + O$	1349

[a] References 3, 4, 9. [b] See text.

barrier, but there is no $\Delta_f H°$ value for neutral $CF_2{=}CFOCF_3$. The dissociation behavior of metastable $CF_2{=}C{=}O^{\bullet+}$ is remarkably similar to that of $CH_2{=}C{=}O^{\bullet+}$ and is therefore likely to be a threshold process. It follows that the available thermochemical data for the reaction

$$CF_2{=}C{=}O^{\bullet+} \xrightarrow{*} CF_2^{\bullet+} + C{\equiv}O \tag{1}$$

should clearly indicate a markedly endothermic process. The $\Delta_f H°$ of $CF_2^{\bullet+}$ appears to be well established with an experimental adiabatic ionization energy (IE_a) of 11.42 eV [4] and $\Delta_f H°[CF_2] = -(205 \pm 12)$ kJ mol^{-1}, which is in agreement with theory.[3] Thus, the product enthalpies for reaction 1 are $\Delta_f H°[CF_2^{\bullet+}] + \Delta_f H°[C{\equiv}O]$ [4] $= [(897 \pm 12) + (-110.5)] = (786 \pm 12)$ kJ mol^{-1}. Thus, the value for $\Delta_f H°[CF_2{=}C{=}O^{\bullet+}]$ must lie below this. Neither $\Delta_f H°[CF_2{=}C{=}O]$ nor its IE appear to be well-established values, there being no entries in the NIST tables.[9]

A value of $\Delta_f H°[CF_2{=}C{=}O]$ was calculated by Zachariah et al.[3] as $-(290 \pm 13)$ kJ mol^{-1}. If the ion lies within a potential well of ≥50 kJ mol^{-1}, then the IE_a is estimated to be ≤10.63 eV. This is not unreasonable if the analogous species $H_2C{=}C{=}CH_2$ ($IE_a = 9.69$ eV)[4,9] and $F_2C{=}C{=}CF_2$ ($IE_a = 10.88$ eV)[4,9] can be used with $CH_2{=}C{=}O$ ($IE_a = 9.63$ eV),[4,9] giving $IE_a[CF_2{=}C{=}O] \approx 10.8$ eV. There are sufficient reference data available to calculate the various product energies for the observed dissociations of $CF_2{=}C{=}O^{\bullet+}$. The relative product energies are shown in Table 1; they are in keeping with the observed mass spectra.

The dissociation of neutral $CF_2{=}C{=}O$ (reaction 2) now deserves attention.

$$CF_2{=}C{=}O \xrightarrow{*} CF_2 + C{\equiv}O \tag{2}$$

The product energies are $\Delta_f H°[C{\equiv}O] = -110.5$ kJ mol^{-1} [4] and $\Delta_f H°[CF_2] = -(205 \pm 12)$ kJ mol^{-1},[4] a sum of -316 kJ mol^{-1}. There appears to be a consensus[1,5] that the perfluoroketene has a barrier to dissociation of ~42 kJ mol^{-1}. If the calculated value[3] $\Delta_f H°[CF_2{=}C{=}O] = -(290 \pm 13)$ kJ mol^{-1} is accepted, the dissociation is exothermic by ~25 kJ mol^{-1}. This reverse energy barrier of some 67 kJ mol^{-1} accounts well for the large kinetic energy release observed for the $CF_2^{\bullet+}$ and $CO^{\bullet+}$ peaks in the NR mass spectrum.

At this point, it is useful to discuss the present state of the available neutral heats of formation of related fluorine-substituted ethene, ketone, allene, and ketene series. The data are presented in Table 2. The first column contains the $\Delta_f H°$ values estimated using Benson's additivity scheme,[13-15] whereas the last column contains the ab initio theoretical values of Zachariah et al.[3] The center column gives values from the compilation of Lias et al.[4] The limitations of the ab initio results are dictated by the characteristics of the model used and by the size of the basis set (i.e., to minimize the calculation time and the round-off error). Benson's additivity results are derived from fixed differences between the constituent groups (e.g., $C_d(H)_2$ to $C_d(F)(H)$ and $C_d(F)(H)$ to $C_d(F)_2$ possess a stabilization energy of -173.1 and -180.3 kJ mol^{-1}, respectively). From Table 2 one can see that Benson's additivity is either reasonably accurate or consistently underestimates the $\Delta_f H°$ value; although generally reliable, the ab initio results have difficulty with the presence of oxygen in the species (e.g., $CF_2{=}O$, $CH_2{=}C{=}O$). On consideration of the above data, the difference between the experimental $\Delta_f H°[CH_2{=}C{=}O]$ [4] and the calculated $\Delta_f H°[CF_2{=}C{=}O]$,[3] namely, about -242.6 kJ mol^{-1} (i.e., the effect of two fluorine substitutions), appears to be anomalously low.

TABLE 2: Relevant Thermochemical Data of Related Unsaturated Species for the Estimation of $\Delta_f H^0[CF_2{=}C{=}O]$

	heat of formation, $\Delta_f H°$ (kJ mol^{-1})		
species	Benson's additivity[a]	standard literature[b]	ab initio theory[c]
ethene series			
$CH_2{=}CH_2$	52.4	(52.2 ± 1.0)	(51.5 ± 4.2)
$CFH{=}CH_2$	−120.7	$-(138.8 \pm 1.7)$	$-(139.2 \pm 6.5)$
$CF_2{=}CH_2$	−301.2	$-(345 \pm 10)$	$-(340.1 \pm 11.0)$
$CFH{=}CF_2$	−474.1	$-(491 \pm 8)$	$-(485.6 \pm 14.0)$
$CF_2{=}CF_2$	−654.4	$-(659 \pm 3)$	$-(653.7 \pm 16.9)$
ketone series			
$CH_2{=}O$	−116.4	$-(108.7 \pm 0.7)$	$-(108.5 \pm 4.2)$
$CFH{=}O$	−380.4	−377[d]	$-(382.3 \pm 4.4)$
$CF_2{=}O$	−644.4	−640	$-(598.4 \pm 7.0)$
allene series			
$CH_2{=}C{=}CH_2$	194.7	(190.6 ± 1.0)	
$CFH{=}C{=}CH_2$	21.6		
$CF_2{=}C{=}CH_2$	−158.7	−202	
$CFH{=}C{=}CF_2$	−331.8		
$CF_2{=}C{=}CF_2$	−512.1	−594	
ketene series			
$CH_2{=}C{=}O$	−47.9	$-(47.7 \pm 2.5)$	$-(40.6 \pm 7.2)$
$CFH{=}C{=}O$	−221.0		$-(147.2 \pm 9.8)$
$CF_2{=}C{=}O$	−401.3		$-(290.3 \pm 13.2)$

[a] References 13−15. [b] Reference 4. [c] Reference 3. [d] Estimated by ref 4.

It seems likely that a revised $\Delta_f H°[CF_2{=}C{=}O]$ value may be significantly lower than the above ab initio value.[3] We believe that the thermochemistry of these species is ripe for reexamination.

Conclusion

Thus, the combined tandem mass spectrometric experimental techniques of MI, CID, and NR indicate that the $C_2F_2O^{\bullet+}$ m/z 78 ion produced from ionized $CF_2{=}CFOCF_3$ is that of a single structure, namely, the perfluoroketene radical cation $F_2C{=}C{=}O^{\bullet+}$. Most importantly, the presence of the neutral $F_2C{=}C{=}O$ as a stable species, possessing a lifetime (about 1 μs) on the order of the transit time between the neutralization cell and the reionization cell in the NR mass spectrum presented here, represents the first direct experimental gas-phase observation of this elusive primary member of the perfluorinated ketenes.

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