carbon-hydrogen bond. Although **3**-C is indicated to be the lowest energy conformer among its set of homomers (31 kcal/mol below **1**-C, 4-31G//STO-3G), the apparent lack of an easy pathway for rearrangement might lend some kinetic stability to **1**-C, if it can be formed. A possible precursor is the pyramidal Hogeveen dication[7] $C_6R_6^{2+}$ which might dissociate to $C_6H_5^+$ and R^+ to reduce electrostatic repulsion. This process would be favorable if R^+ is a stable cation (e.g., *tert*-butyl). The $C_6R_5^+$ thus formed might be expected to retain the pyramidal structure of this dication.

We have not proven that **1**-Si is the most stable $C_5H_5Si^+$ isomer, but this seems likely. It would seem imperative to place as much of the excess positive charge as possible on Si, but in alternative noncyclic structures this must lead to a structure with unfavorable Si–C multiple bonding. Although the energy estimates provided here may be only qualitatively correct, the geometries obtained should be reasonably reliable[33] and will be useful as starting points for higher level calculations (e.g., those combining split valence and d basis sets), when these become feasible.

Acknowledgment. We gratefully acknowledge the cooperation provided by the Regional Computation Center in Erlangen and the availability of an efficient geometry optimization program written by D. Poppinger and a single-precision version of GAUSSIAN 70 for the TR440 computer written by H.-U. Wagner. We thank M.-B. Krogh-Jespersen and E. D. Jemmis for valuable discussions and W. J. Hehre and J. A. Pople for supplying the 3-21G basis sets prior to publication. This work was supported by the Fonds der Chemischen Industrie at Erlangen and by a Merck Junior Faculty Development Grant at Rutgers.

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Gaseous Anion Chemistry. Negative Chemical Ionization of Acyl Chlorides, Diacyl Chlorides, and Perfluorodiacyl Chlorides

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We report here reactions of OH^- and $O^-\cdot$ in the gas phase with seven acyl chlorides, three diacyl chlorides, and two perfluorodiacyl chlorides through examination of negative chemical ionization mass spectra. With OH^- as the reactant, formation of the acetylenic alkoxide ion, $RC{\equiv}CO^-$, is favored. Reactions with $O^-\cdot$ typically are simpler than those with OH^- and show Cl^- as the most intense ion. In neither case are $(M - 1)^-$ ions or ions containing chlorine seen. The intensity of $O^-\cdot$ spectra varies widely with structure. The reactions of perfluorosuccinyl and perfluoroglutaryl chloride are quite different from their nonfluorinated analogues, and loss of the elements of phosgene is an important process. There is some evidence for occurrence of intramolecular hydrogen transfer with $O^-\cdot$ as the reactant ion.

In recent years there have appeared the first reports of OH^- negative chemical ionization mass spectra of various types of organic compounds, including simple esters, ketones, and alcohols,[1] essential oils,[2] steroids,[3] methadone and its metabolites,[4] and both cyclic[5] and open-chain[6] diols. In the present study we have examined both the OH^- and the $O^-\cdot$ spectra of seven simple acyl chlorides, three straight-chain diacyl chlorides, and two perfluorodiacyl chlorides. Our studies have served to identify interesting chemical transformations brought about by anions in the gas phase, and these are discussed below.

When OH^- was used as the ionizing reagent, it was produced by reactions of $O^-\cdot$ from N_2O (eq 1) with either hydrogen or methane, following eq 2 or 3. The same methods have been used in previous studies in this laboratory.[1-3,6] When the ionizing reagent was $O^-\cdot$, it was produced from N_2O as shown in eq 1. We have previously suggested that the other processes involving N_2O in this system are those summarized in eq 4–9, where reaction 9

$$N_2O + e \rightarrow N_2 + O^-\cdot \tag{1}$$

$$O^-\cdot + H_2 \rightarrow OH^- + H \tag{2}$$

$$O^-\cdot + CH_4 \rightarrow OH^- + CH_3 \tag{3}$$

$$O^-\cdot + N_2O \rightarrow [N_2O_2^-\cdot]^* \tag{4}$$

$$[N_2O_2^-\cdot]^* \rightarrow O_2^-\cdot + N_2 \tag{5}$$

$$[N_2O_2^-\cdot]^* \rightarrow NO^- + NO \tag{6}$$

$$[N_2O_2^-\cdot]^* + N_2O \rightarrow NO_2^- + NO + N_2 \tag{7}$$

$$[N_2O_2^-\cdot]^* + N_2O \text{ (or M)} \rightarrow N_2O_2^-\cdot + N_2O \text{ (or M)} \tag{8}$$

$$X^- \rightarrow X + e \tag{9}$$

is any electron-loss process that may take place.[6] We have discussed our reasons for preferring this scheme to that discussed earlier by Caledonia.[7] Also, we have noted[6] that we have no way of ascertaining whether spectra determined in N_2O alone result specifically from reaction of $O^-\cdot$ with the substrate molecule or alternatively arise through transfer of $O^-\cdot$ to the molecule from some other species, presumably NO_2^-, that is formed in reactions 4–9. For convenience and simplicity, however, we discuss these

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[1] Smit, A. L. C.; Field, F. H. *J. Am. Chem. Soc.* **1977**, *99*, 6471.

[2] Bruins, A. P. *Anal. Chem.* **1979**, *51*, 967.

[3] Roy, T. A.; Field, F. H.; Lin, Y. Y.; Smith, L. L. *Anal. Chem.* **1979**, *51*, 272.

[4] Smit, A. L. C.; Field, F. H. *Biomed. Mass Spectrom.* **1978**, *5*, 572.

[5] Winkler, F. J.; Stahl, D. *J. Am. Chem. Soc.* **1978**, *100*, 6779.

[6] Lloyd, J. R.; Agosta, W. C.; Field, F. H., submitted for publication in *J. Am. Chem. Soc.*

[7] Caledonia, G. E. *Chem. Rev.* **1975**, *75*, 333.

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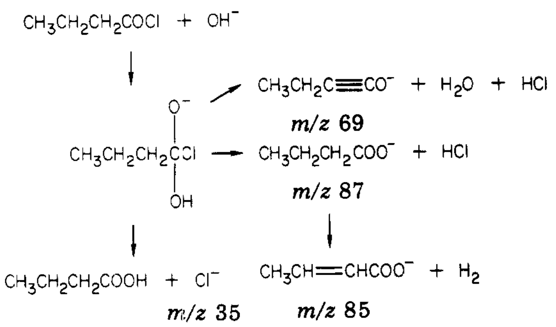
Table I. OH^- Negative Chemical Ionization Mass Spectra[a] of Simple Acyl Chlorides

compd	mol wt[c]	ΣI[d]	mass and relative intensities,[b] m/z (RI)					
			$(M-19)^-$ $[(M+OH-HCl)^-]$	$(M-21)^-$ $[(M+OH-HCl-H_2)^-]$	$(M-37)^-$ $[(M+OH-HCl-H_2O)^-]$	$(2M-73)^-$ $[(2M+OH-2HCl-H_2O)^-]$	Cl^- [e]	other ions
acetyl chloride	78	4800	59 (24)		41 (63)		(13)	
propionyl chloride	92	4600	73 (21)	71 (4)	55 (56)		(19)	
butyryl chloride	106	3800	87 (18)	85 (4)	69 (48)	139 (10)	(20)	
valeryl chloride	120	4600	101 (34)	99 (9)	83 (43)	165 (5)	(8)	
caproyl chloride	134	4700	115 (27)	113 (7)	97 (50)	195 (7)	(6)	
isobutyryl chloride	106	11000	87 (18)	85 (7)			(72)	95 (2), 68 (1)
trimethylacetyl chloride	120	10000	101 (15)				(80)	81 (5)

[a] P_{N_2O} = 2.0 torr, P_{CH_4} = 1 torr, source temperature 210 °C. [b] Relative intensities as a percentage of total ionization attributed to sample. [c] Cl = 35 daltons. [d] Absolute intensity in arbitrary units. [e] Sum of m/z 35 and 37, which are in approximately a 3:1 ratio.

Scheme I



spectra in terms of direct attack by $O^{-}\cdot$. Also for simplicity, molecular weight calculations for ions and molecules are based only on the more abundant chlorine isotope, ^{35}Cl.

$O^{-}\cdot$ spectra were determined by adding ~0.5 μL of the acyl chloride of interest through the gas-handling system of the mass spectrometer to 1.5 torr of N_2O at approximately 210 °C. After the $O^{-}\cdot$ spectrum was recorded, 1.0 torr of CH_4 or H_2 was admitted to the system, and the OH^- spectrum was determined. Thus, the two types of spectra were determined under comparable conditions. Acyl chlorides are somewhat difficult to prepare and maintain in high purity. The lower molecular weight compounds particularly are prone to hydrolysis by adventitious water with formation of hydrogen chloride and the corresponding carboxylic acid, which itself reacts with a second molecule of the acyl halide to yield more hydrogen chloride and the anhydride. For this reason some portion of the Cl^- and carboxylate anions seen in these spectra may arise from attack of OH^- or $O^{-}\cdot$ on hydrogen chloride and on the symmetrical anhydride or carboxylic acid, respectively. In determining the spectra of acetyl and propionyl chloride, we noted a memory effect, in that Cl^- could be detected after the sample has been pumped out and N_2O–CH_4 reintroduced into the system. We tentatively attribute this behavior to ionization of residual hydrogen chloride adsorbed in the gas-handling system. This problem could be avoided by flushing out the system carefully before reintroduction of N_2O–CH_4. It was not encountered with the higher molecular weight substrates.

Experimental Section

The apparatus and techniques used for this work were very similar to those described by Smit and Field[1]. The mass spectrometer was a Biospect quadrupole mass spectrometer manufactured by Scientific Research Instruments. The instrument was modified for negative-ion detection by using the negative-ion detection system previously developed in this laboratory. The output signal from the mass spectrometer was introduced into a VG2040 data system for recording and storage of the mass spectra. The scan rate was such that 2 s was required to scan from zero mass to whatever upper mass limit was appropriate to the experiment being undertaken. Ionization was initiated by bombardment with electrons emitted from a filament; the emission current was maintained at 200 μA. The reagent gas consisted of 1.5 torr of nitrous oxide and 1.0 torr of either hydrogen or methane. Samples were introduced through the gas-handling system of the mass spectrometer, and a rough measure of the relative amounts of sample present in the ionization chamber was provided by measuring the volume in microliters of liquid sample injected into the gas-handling system.

All measurements reported in this paper were replicated at least once.

The reagent gases used were obtained from Matheson Gas Products and were of an appropriately high degree of purity: nitrous oxide, 98.5%; hydrogen, 99.95%; methane, 99.97%. All acyl halides were nominally 97% pure. They were obtained from the indicated suppliers: perfluorosuccinyl chloride and perfluoroglutaryl chloride, PCR Research Chemicals, Inc.; acetyl chloride, Matheson Coleman and Bell; all other acyl halides, Aldrich Chemical Co.

Results and Discussion

Spectra of Simple Acyl Chlorides. In Table I we give the OH^- negative chemical ionization spectra, obtained in N_2O–CH_4, of the straight-chain acyl chlorides with two through six carbon atoms and the branched-chain compounds, isobutyryl chloride and trimethylacetyl (pivalyl) chloride. The straight-chain compounds all give analogous

Scheme II

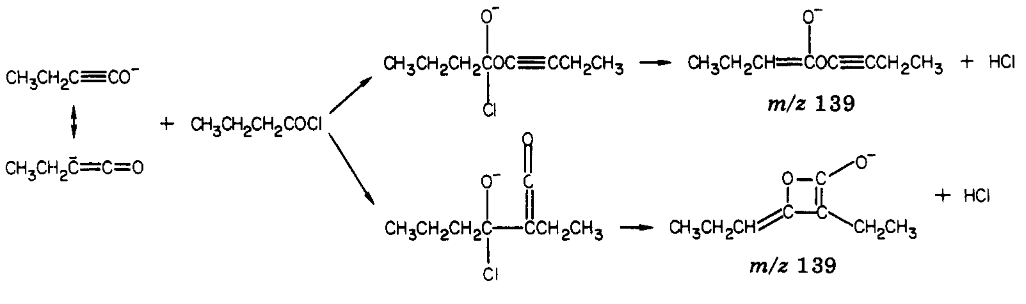
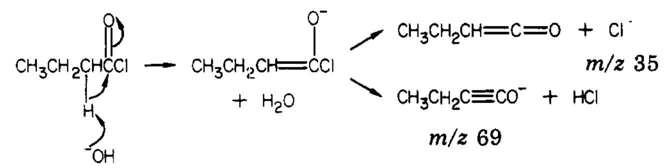


Table II. $O^{-}\cdot$ Spectra[a] of Simple Acyl Chlorides

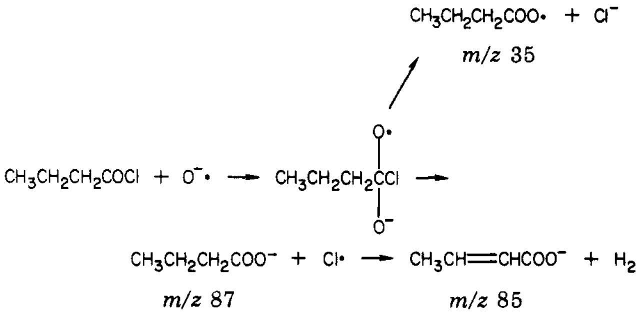
compd	mol wt[c]	ΣI[d]	mass and relative intensities,[b] m/z (RI) $(M-19)^-$ $[(M+O-Cl)^-]$	$(M-21)^-$ $[(M+O-Cl-H_2)^-]$	Cl^- [e]	other ions
acetyl chloride	78	800	59 (8)		(92)	
propionyl chloride	92	600	73 (26)	71 (16)	(57)	
butyryl chloride	106	800	87 (32)	85 (42)	(26)	
valeryl chloride	120	500		99 (100)		
caproyl chloride	134	600		113 (100)		
isobutyryl chloride	106	9600	87 (4)	85 (5)	(84)	68 (7)
trimethylacetyl chloride	120	7200	101 (6)		(94)	

[a] P_{N_2O} = 2.0 torr, source temperature 210 °C. [b] Relative intensities as a percentage of total ionization attributed to sample. [c] Cl = 35 daltons. [d] Sum of the absolute intensities attributed to sample in arbitrary units. [e] Sum of m/z 35 and 37, which are in approximately a 3:1 ratio.

Scheme III



Scheme IV



results, and we will discuss only the spectrum of butyryl chloride. A particularly interesting finding is that the most intense ion is not Cl^-, as might have been expected, but rather the ion at m/z 69, $(M + OH - HCl - H_2O)^-$. Pathways by which the observed ions may be formed and suggested structures for these species are shown in Schemes I and II. These pathways permit derivation of reasonable structures for the observed ions from a common intermediate formed on addition of OH^- to the carbonyl group.

Straightforward loss of Cl^- or HCl from this initial ion leads to ions at m/z 35 and 87, respectively. The additional loss of H_2 with formation of the ion at m/z 85 is shown leading to an α,β-double bond. There is no evidence for this choice, although this position for the unsaturation should be energetically favorable through conjugation with the carboxylate group and disubstitution of the double bond. The simplest formulation of the intense m/z 69 ion is the acetylenic alkoxide (or ketene enolate) anion shown. Formation of this unusual species from the initial adduct ion requires the novel vicinal elimination of both HCl and H_2O. Attack of this alkoxide ion on a second molecule of acyl halide and subsequent elimination of HCl can lead to the low-intensity association ion at m/z 139. As shown in Scheme II, two possible formulations for this ion are the ester enolate and conjugated lactone enolate anions that can be derived through the two different modes of addition of the acetylenic alkoxide to a second molecule of butyryl chloride. As required for such a second-order process, the relative intensity of this ion increases much more rapidly with the concentration of butyryl chloride than do the relative intensities of the ions at m/z 69 and 87.

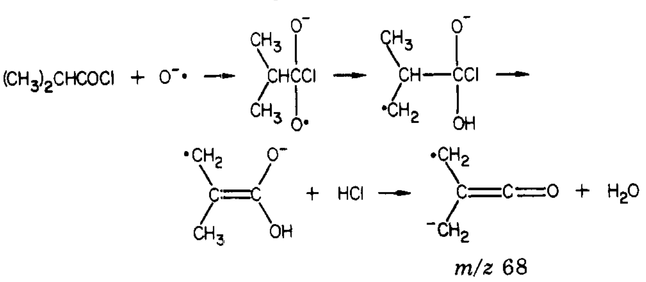
An alternative possibility that could account for part or all of the Cl^- and m/z 69 ions is depicted in Scheme III. This requires initial deprotonation of butyryl chloride by OH^-, followed by loss of Cl^- or HCl from the enolate anion. There is no direct evidence against participation of this pathway, but the greater relative intensity of the Cl^- ion in the spectrum of trimethylacetyl chloride, where there is no removable α proton, suggests that the addition mechanism given in Scheme I is responsible for at least a portion of the Cl^- formed from butyryl chloride. Furthermore, formation of the adduct ion of Scheme I seems specifically to be required to account for the ions at m/z 87 and 85.

It will be seen in Table I that the two branched-chain halides furnish no ions analogous to the ions at m/z 69 and 139 in the butyryl chloride spectrum and that similarly there is no ion corresponding to m/z 85 from either acetyl chloride or trimethylacetyl chloride. These results are consistent with the scheme and structures for the ions from butyryl chloride discussed above. In addition to the ions in Schemes I and II there is an ion of low intensity at m/z 95 in isobutyryl chloride and one at m/z 81 in trimethylacetyl chloride that we cannot explain. The ion at m/z 68 from isobutyryl chloride is discussed with the $O^-\cdot$ spectra below. This ion increases in relative intensity from 1% in the OH^- spectrum to 7% in the $O^-\cdot$ spectrum, and we believe that in the OH^- spectrum it probably also results from reaction of $O^-\cdot$ with the halide. This proposal requires that isobutyryl chloride compete successfully with methane (eq 3) for reaction with $O^-\cdot$ or its equivalent. We have previously noted examples of ions of low intensity from addition of $O^-\cdot$ in spectra obtained in the presence of OH^-.[6]

The ionization of these acyl chlorides by OH^- may be contrasted with the previously reported behavior of simple esters,[1] where the most important ions are $(M - 1)^-$ and the carboxylate anion, and the alkoxide ion is generally weak or absent. As we noted above, we cannot distinguish between addition and deprotonation as two possible modes of initial reaction of OH^- with the straight-chain acyl halides. The absence of the $(M - 1)^-$ ion in these spectra may indicate that this ion is formed but rapidly eliminates Cl^- (Scheme III). That is, since Cl^- is more stable than alkoxide ion, the $(M - 1)^-$ ion may be stable in esters but unstable in acyl chlorides. Alternatively, the absence of $(M - 1)^-$ may indicate that addition of OH^- to the carbonyl group competes successfully with deprotonation in acyl chlorides but not in esters and that this difference results from a more reactive carbonyl group in acyl chlorides.

In Table II we summarize the $O^-\cdot$ spectra of these seven acyl chlorides. It will be seen that these spectra are simpler, generally consisting of only three ions. The formation of these ions can be explained by the reactions given in

Scheme V



Scheme IV, where butyryl chloride is once again used as the example. The absence of the ions at m/z 69 and 139 that are found in the OH^- spectrum is noteworthy and plausible. Formation of the ion at m/z 69 requires loss of H_2O and HCl from the OH^- adduct ion (Scheme I) and would analogously require loss of OH· and HCl from the O^-· adduct (Scheme IV). The heats of formation of H_2O and OH· are −58 and +9 kcal/mol, respectively,[8] and thus removal of H_2O is more exothermic by 67 kcal/mol than loss of OH· would be.

Another interesting feature of the O^-· spectrum is that the ratio I_{85}/I_{87} has increased in comparison with the ratio in the OH^- spectrum. That is, there is more loss of H_2 with O^-· as the reactive anion than there is with OH^-. As indicated in Schemes I and IV, we assume that this loss of H_2 occurs from the carboxylate anion, $(M - 19)^-$; enhancement of this process in the O^-· spectra can be explained by energetic considerations. Using the known[8] heats of formation of OH^- (−33), O^-· (+25), Cl· (+29), and HCl (−22 kcal/mol), we calculate that the energy released in eq 10 is 7 kcal/mol greater than that in eq 11, and

$$RCOCl + O^{-}\cdot \rightarrow RCOO^{-} + Cl\cdot \quad (10)$$

$$RCOCl + OH^{-} \rightarrow RCOO^{-} + HCl \quad (11)$$

consequently we expect that the energy content of the carboxylate ion in (10) will be greater than that in (11). The more energetic carboxylate ion should lose H_2 more readily.

The unique even-mass ion at m/z 68 in the spectrum of isobutyryl chloride presents a problem. The composition of this ion must be $C_4H_4O^-$·, necessitating loss of HCl and H_2O from the initial adduct, and this must occur from a species that initially has no hydrogen bound to oxygen. We suggest that intramolecular hydrogen transfer takes place. This process is already well established for electron-deficient oxygen species in the McLafferty rearrangement observed in positive ions of carbonyl compounds,[9] in the reactions of alkoxy radicals generated in solution,[10] and in the photochemical type II rearrangement.[11] In general, six-membered intermediates are favored in such processes, but both smaller and larger intermediates are sometimes seen. In the present case only a five-membered intermediate is possible, and the suggested steps leading to m/z 68 are shown in Scheme V.

Four phenomena indicated by the data in Tables I and II are worthy of further comment. First, the Cl^- intensity in the O^-· spectra (Table I) decreases sharply along the series of straight-chain halides. While we recognize that the problem of hydrolysis of the lower members of the series, as mentioned above, may contribute to the differences observed, we do not believe this is the sole explanation. In addition, it will be seen that the intensity of Cl^- in both the O^-· and OH^- spectra of isobutyryl chloride and trimethylacetyl chloride is much greater than the Cl^- intensity in the straight-chain compounds. We do not yet understand this phenomenon; we have investigated the possibility that these two branched-chain compounds are subject to thermal decomposition under our experimental conditions but have not found this to be the case. The third phenomenon of interest concerns absolute intensities of total ionization. From Table II we note that the intensities for the straight-chain compounds are on the order of 10 times smaller than those of the branched-chain isomers. From Table I we seen that with OH^- as the reactant a similar trend in intensities occurs, but the difference now is a factor of 2–3. For both reactant ions the larger total ionization in the branched compounds is largely due to enhanced production of Cl^-. Finally, a comparison of Tables I and II shows a strikingly lower total ionization in the O^-· spectra of the straight-chain compounds. We have no satisfactory explanation for these phenomena and believe that they warrant future study.

Table III. OH^- Negative Chemical Ionization Mass Spectra[a] of Diacyl Chlorides

compd	mol wt	ΣI	mass and relative intensities, m/z (RI)		
			$(M - 55)^-$ $[(M + OH - 2HCl)^-]$	$(M - 99)^-$ $[(M + OH - 2HCl - CO_2)^-]$	Cl^-
malonyl chloride	140	3400		41 (79)	(21)
succinyl chloride	154	5000	99 (81)		(19)
glutaryl chloride	168	4300	113 (87)		(13)

[a] Same conditions and notation as Table I.

Spectra of Diacyl Chlorides. The results gathered in Table III indicate that the presence of a second acyl chloride group in the substrate molecule profoundly changes its OH^- negative-ion spectrum. There is about the same amount of Cl^- as in the simple acyl chlorides, but all other ions previously seen are replaced by the m/z 99 ion in succinyl chloride, by the homologous m/z 113 ion in glutaryl chloride, and by an m/z 41 ion in malonyl chloride. Pathways and structures that explain these observations are shown in Scheme VI for the three compounds of interest. The cyclic intermediates shown are not required by our results, but they do provide a convenient rationalization for the observed loss of HCl from both ends of the molecule. A deprotonation mechanism like that given in Scheme III can also be written to account for some or all of the Cl^- formed here. The unique behavior of malonyl chloride is understandable on the basis of the structures suggested for the ions. The ketene carboxylate $(M - 55)^-$ ions should be relatively stable in the two longer chain species, since decarboxylation would leave the negative charge localized on a simple methylene group. Only in malonyl chloride can decarboxylation lead to the resonance-stabilized alkoxide ion, m/z 41. It is interesting that it is mechanistically attractive to formulate this as the same type of acetylenic alkoxide reached in a different fashion in the case of the simple acyl halides above.

The O^-· spectra of the dicarboxylic acid derivatives are given in Table IV. These spectra are quite weak, as were the O^-· spectra of the straight-chain monoacyl chlorides.

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[8] Rosenstock, H. M.; Draxl, K.; Steiner, B. M.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl. 1* 1977, *6*.

[9] Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day: San Francisco, 1967; Chapter 3.

[10] For example, Akhtar, A. *Adv. Photochem.* **1964**, *2*, 263.

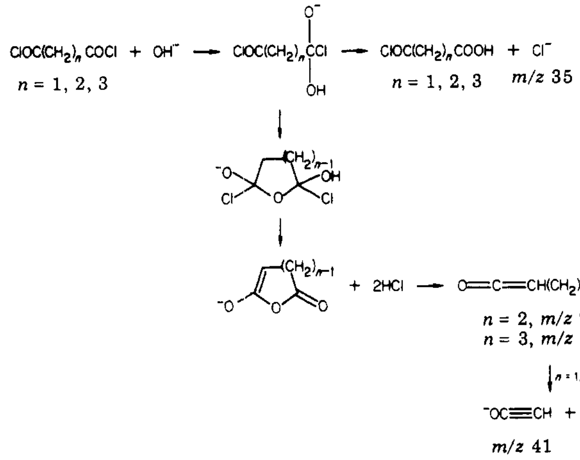
[11] Wagner, P. J. *Acc. Chem. Res.* 1971, *4*, 1681 and references cited therein.

Table IV. $O^{-}\cdot$ Spectra[a] of Diacyl Chlorides

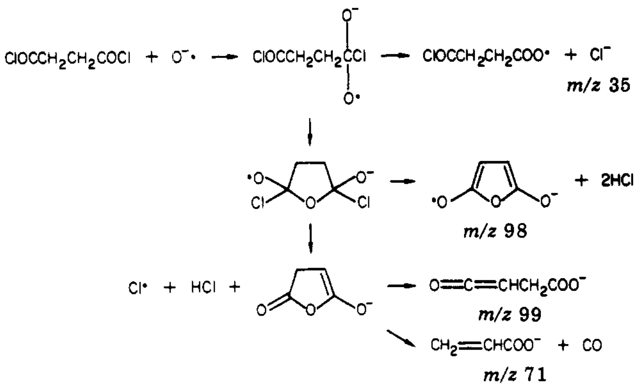
compd	mol wt	ΣI	mass and relative intensities, m/z (RI): $(M - 55)^-$ $[(M + O - HCl - Cl)^-]$	$(M - 56)^-$ $[(M + O - 2HCl)^-]$	$(M - 83)^-$ $[(M + O - HCl - Cl - CO)^-]$	Cl^-	other ions
malonyl chloride	140	260				(100)	
succinyl chloride	154	630	99 (3)	98 (4)	71 (4)	(86)	73 (1), 64 (2)
glutaryl chloride	168	720			85 (7)	(85)	

[a] Same conditions and notation as Table II.

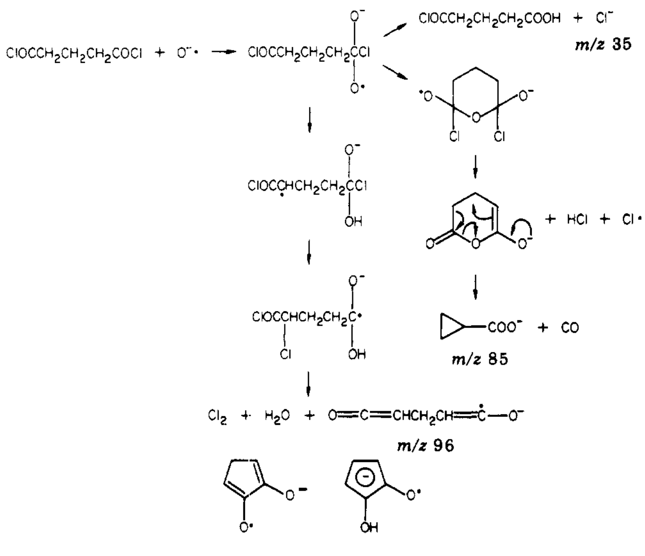
Scheme VI



Scheme VII



Scheme VIII



In these dichlorides the most intense ion is Cl^-. No other ions are seen from malonyl chloride, but several weak ions are seen in the higher homologues. A rationalization for some of these in succinyl chloride is given in Scheme VII. Cyclization of the initial adduct ion and subsequent loss of two molecules of HCl can furnish a radical anion at m/z 98 that benefits from the aromaticity of the furan ring. The corresponding homologous ion from glutaryl chloride would not be aromatic, and, in fact, no such ion is seen. Alternatively, the cyclic intermediate could lose HCl and a chlorine atom and yield, after ring opening, the ketene carboxylate anion, m/z 99. Loss of CO concomitant with ring cleavage could furnish acrylate anion, m/z 71.

In Scheme VIII a similar set of transformations is shown for glutaryl chloride to account for ions at m/z 35 and 85. The even-mass ion at m/z 96 has no counterpart in the spectrum of succinyl chloride, and we outline a pathway to account for its formation that involves a hydrogen transfer similar to that discussed above. In this case a six-membered intermediate is possible, following the usually preferred path for such abstractions. The initial hydrogen transfer is followed by a chlorine transfer and loss of Cl_2 and H_2O to yield m/z 96. Cyclization of the linear radical anion could give a cyclopentadiene; intramolecular hydrogen transfer before cyclization could provide the resonance-stabilized cyclopentadienide. Both these possible isomeric ions are shown.

Spectra of Perfluorodiacyl Chlorides. Finally in Table V we present the spectra of perfluorosuccinyl and perfluoroglutaryl chloride. These compounds give essentially the same mass spectra when N_2O–H_2, N_2O–CH_4, or N_2O alone is used, and we believe that under all these sets of conditions the initial reaction is addition of $O^{-}\cdot$ to the diacyl chloride. The data in Table VI support this suggestion; these show the change in the N_2O–CH_4 spectrum brought about by introduction of 1.0 μL of perfluorosuccinyl chloride. The ions derived from N_2O, largely by way of reactions 1, 2, and 4–9, are reduced in overall intensity on addition of the acyl halide by approximately the same amount as the total intensity of the ions produced in the acyl halide spectrum. In contrast, the decrease in OH^- ion under these circumstances is only about 35% of the intensity of the acyl halide spectrum. This effect may be contrasted with that typically observed upon addition to this system of a substrate that undergoes only deprotonation by OH^-, such as a simple enolizable ketone.[1] In this latter case the reduction in OH^- ion is approximately the same as the intensity of the $(M - 1)^-$ produced from that added substrate. This difference in behavior in the two cases suggests that the perfluoroacyl chloride competes successfully with CH_4 for reaction with $O^{-}\cdot$ and that this reaction is responsible for much, if not all, of the ionization produced. In keeping with this suggested unusual reactivity toward $O^{-}\cdot$, the spectra of these perfluoro compounds are much more intense than the $O^{-}\cdot$ spectra of the related ordinary diacyl chlorides (Table IV). We suggest

Table V. OH^- Negative Chemical Ionization Spectra[a] of Perfluorodiacyl Chlorides

compd	mol wt	ΣI	mass and relative intensities, m/z (RI) $(M - 82)^-$ $[(M + O - COCl_2)^-]$	$(M - 145)^-$ $[(M + O - COCl_2 - CO_2 - F)^-]$	Cl^-	F^-
perfluorosuccinyl chloride	226	5300	144 (66)	81 (3)	(24)	(7)
perfluoroglutaryl chloride	276	4300	194 (60)	131 (2)	(30)	(8)

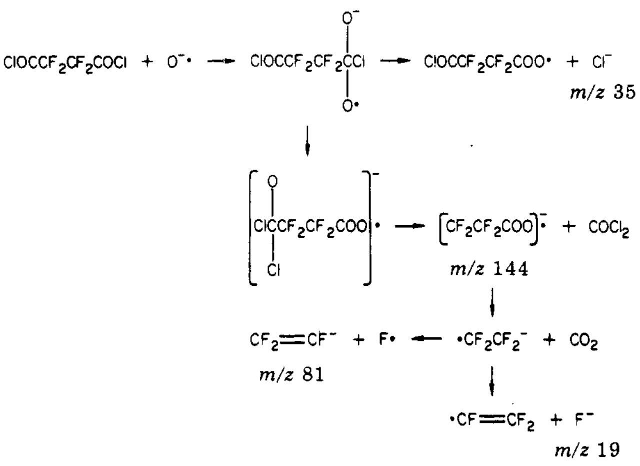
[a] Same conditions and notation as Table I.

Table VI. OH^- Negative Chemical Ionization[a] Spectrum of Perfluorosuccinyl Chloride

	A. ions derived from N_2O[b]			B. N_2O-derived ions after addition of perfluorosuccinyl chloride			C. perfluorosuccinyl chloride ions		
	m/z	AI[c]	RI[d]	m/z	AI	RI	m/z	AI	RI
OH^-	17	3584	52	17	1736	82	19	415	7
CN^-	26	359	5	26	0	0	35	945	18
$O_2^-\cdot$	32	1320	19	32	227	11	37	315	6
$HO^-\cdot H_2O$ and/or Cl^-	35	676	10	35	159	7	81	136	3
N_3^- or CNO^- ?	42	399	6	42	0		144	3509	66
NO_2^-	46	91	1	46	0				
$N_2O_2^-$?	60	215	3	60	0				
?	61	193	3	61	0				
sum[e]		6837	99		2122	100		5320	100

[a] P_{N_2O} = 1.0 torr, P_{CH_4} = 1 torr, source temperature 210 °C. [b] Products of $O^-\cdot$ reactions with N_2O/CH_4. [c] Absolute intensity. [d] Relative intensity. [e] Sum of the AI or RI values in the column above.

Scheme IX



that this increased reactivity is due to reduced electron density on the carbonyl carbons effected by the electronegativity of the adjacent CF_2 groups.

An alternative possibility to be considered is that some or all of the ions in these spectra are attributable to resonance-capture processes, since some perfluorinated organic compounds undergo electron capture with facility.[12] For investigation of this point, perfluorosuccinyl chloride was introduced into the source with 2 torr of CH_4 as a stopping gas. No ions were observed under these conditions. Since similar conditions do yield electron-capture spectra of nitrobenzene and, of course, of N_2O, we conclude that the spectra recorded in Table V result from $O^-\cdot$ addition and not electron capture.

It is most interesting that the most abundant ion formed in these spectra is not Cl^- or F^- but the ion $(M - 82)^-$ that results from loss of the elements of phosgene from the initial $O^-\cdot$ adduct $(M + O - COCl_2)^-$. In Scheme IX we present mechanisms that can account for the four ions observed in perfluorosuccinyl chloride. Analogous structures and pathways can be written for the ions from the higher homologue. We account for the m/z 144 ion through 1,4 migration of Cl· or Cl^- followed by cleavage and loss of phosgene, while subsequent decarboxylation of this m/z 144 ion can give an intermediate that furnishes both the F^- and m/z 81 ions. In Scheme VII we suggested the reaction of succinyl chloride through cyclization to a furan derivative, followed by loss of HCl. We believe that the quite different behavior of the perfluoro derivative results from the fact that the analogous reaction now would require loss of FCl. We think that the very high strength of C–F bonds makes this unlikely.

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Registry No. Acetyl chloride, 75-36-5; propionyl chloride, 79-03-8; butyryl chloride, 141-75-3; valeryl chloride, 638-29-9; caproyl chloride, 142-61-0; isobutyryl chloride, 79-30-1; trimethylacetyl chloride, 3282-30-2; malonyl chloride, 1663-67-8; succinyl chloride, 543-20-4; glutaryl chloride, 2873-74-7; perfluorosuccinyl chloride, 356-15-0; perfluoroglutaryl chloride, 678-77-3.

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[12] Hunt, D. F.; Stafford, G. C., Jr.; Crow, F. W.; Russell, J. W. *Anal. Chem.* **1976**, *48*, 2098.