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Low Pressure Gas-phase Reactions of the Atomic Oxygen Radical Anion with Halomethanes Studied Using Fourier Transform Ion Cyclotron Resonance

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The gas-phase reactions of the O^- radical anion with the halomethanes CH_3X , CH_2X_2 , CHX_3 , CX_4 , CF_3X , CF_2X_2 , CFX_3 ($X = Br$ and Cl) and $CXCIBr_2$ ($X = Cl$ and F) have been examined at a low pressure (10^{-5} – 10^{-4} Pa) with use of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. The overall reactions proceed essentially with the collision rate and lead to a variety of product ions dependent on the number and nature of the halogen atoms present in the substrate. For CH_3Cl and CH_3Br , the dominant pathways are H abstraction, H_2^{+} abstraction and nucleophilic substitution. With CH_2Cl_2 , proton transfer is an additional major pathway and in the reaction with CH_2Br_2 attack on a halogen atom with formation of BrO^- ions also occurs. In the reactions with $CHCl_3$ and $CHBr_3$, proton transfer competes with attack on a halogen atom, whereas initial attack on a halogen atom dominates in the reactions of O^- with the CCl_4 and CBr_4 methanes. Attack on the carbon atom is the main process if CF_3Cl is the substrate and results in F^- , Cl^- as well as FCl^- ions. For CF_3Br , however, attack on the bromine atom with formation of BrO^- ions dominates over the reaction at the carbon atom. In the reactions with CF_2Cl_2 , $CFCl_3$, CF_2Br_2 and $CFBr_3$ as well as the CCl_2Br_2 and $CFCIBr_2$ methanes, most product ions are formed by competing attack on a chlorine and bromine atom. For some of the halomethanes, the present findings are compared with reported results obtained with use of the high pressure (≈ 70 Pa) flowing afterglow and selected ion flow tube methods. © 1997 by John Wiley & Sons, Ltd.

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The gas-phase ion/molecule chemistry of the atomic oxygen radical anion is of special interest as indicated by the large number of studies concerned with the reactions of this species.^{1–3} In particular, a number of studies have been concerned with the gas-phase ion/molecule reactions of the O^- ion with halomethanes^{4–11} owing, in part, to the fundamental importance of these processes and, in part, to the possible occurrence of reactions between negative ions such as the O^- ion and fluorocarbons in the upper atmosphere.^{12–14} Most of these studies have been performed with use of the high pressure (≈ 70 Pa of helium bath gas) flowing afterglow (FA) or the selected-ion flow tube (SIFT) methods¹⁵ and have been concerned with the reactions of O^- as well as O_2^- with a relatively limited number of halomethanes. Notably, the kinetics of the reactions of the O^- ion with CH_3Cl and CH_3Br were examined by Tanaka *et al.* with use of the FA method,⁵ whereas Dotan *et al.* studied the reactions of O^- with a number of chlorine-containing molecules including CCl_4 .⁶ The reactions with halomethanes such as CF_3Br and CF_2ClBr have also been examined, even though the experimental conditions did not allow for a distinction to be achieved between the product ions formed in the reactions of the O^- and O_2^- radical anions.⁷ A more thorough study has been published by Morris, who applied the SIFT technique in order to study separately the reactions of the O^- and O_2^- ions with CF_4 , CF_3Cl , CF_3Br , CF_3I and C_2F_4 at temperatures of 300 K and 500 K, respectively.⁹ More recently, Mayhew *et al.* reported the product-ion

distributions and the kinetics of the reactions of the O^- and O_2^- ions with the complete series of chloromethanes and chlorofluoromethanes at 300 K as determined with use of the SIFT method.¹⁰

The general outcome of these studies is to show that the O^- ion displays a relatively complicated chemistry in its reactions with halomethanes which may involve proton transfer, hydrogen atom abstraction, formal H_2^{+} abstraction as well as attack on either the carbon atom or a halogen atom. Notwithstanding the results given in the previous studies, a systematic examination of the product-ion distributions of the reactions of the O^- ion with the full series of chloro- and bromomethanes as well as the related chlorofluoro- and bromofluoromethanes has not appeared. This prompted us to report upon these product-ion distributions as obtained with the use of a single instrument. To this end we applied the low pressure Fourier transform ion cyclotron resonance (FTICR)¹⁶ method, thus allowing a comparison with the results obtained for some of the selected halomethanes at the higher pressures typical of FA or SIFT instruments.¹⁵

EXPERIMENTAL

The experiments were performed with an FTICR instrument designed and constructed at the University of Amsterdam.¹⁷ In a typical experiment,^{18,19} the O^- radical anions were formed by dissociative capture of electrons with an energy of ≈ 1.2 eV by nitrous oxide for a period of 150 ms and trapped in a magnetic field of 1.23 T by applying a small negative voltage (≈ -1 V) to the trapping plates of the cubic-inch sized FTICR

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cell. The O^{-•} radical anions were subsequently isolated by ejecting all other ions from the cell, as described previously.¹¹ The reactions of the O^{-•} ion with a given halomethane were then followed as a function of time by varying the delay between the selection of the O^{-•} ion and the start of the excitation pulse.

For the majority of the halomethanes included in the present study, abundant Cl⁻ and/or Br⁻ ions were generated by dissociative electron attachment. The formation of halide ions by capture of low-energy electrons during the period in which the O^{-•} ions were allowed to react with a given halomethane was suppressed by ejecting these electrons from the FTICR cell.²⁰ Most experiments were performed with a low partial pressure of nitrous oxide; that is, the majority of the results were obtained with a ratio between the partial pressures of N₂O and the halomethane of 1:10, the total pressure being about 3×10^{-5} Pa. The low partial pressure of nitrous oxide was chosen in order to suppress the reaction of O^{-•} with this neutral species. This reaction is known to yield free electrons and also relatively abundant NO⁻ ions,^{21,22} which may react further with the halomethanes.^{23,24} A second series of experiments was performed with a higher pressure of nitrous oxide in order to examine the influence of the pressure of this neutral species on the product ion distributions. In these experiments, the ratio between the partial pressures of nitrous oxide and a halomethane was 1:1, the total pressure being $\approx 5 \times 10^{-5}$ Pa. In addition, the NO⁻ ions were ejected continuously from the cell during the entire reaction period in these experiments.

The pressures were measured with an uncalibrated ionization gauge placed in the side arm of the main pumping line. The inlet lines and the main vacuum vessel were at room temperature, whereas the temperature of the trapping plate opposite to the filament was between 330 and 340 K in a typical experiment. All the chemicals used were commercially available and used without purification except for CHBr₃ which was distilled before use.

RESULTS

The atomic oxygen radical anion is reported to react with the complete series of chloromethanes at essentially the collision rate.¹⁰ A similar situation applies to the reactions of the O^{-•} ion with CF₂Cl₂ and CFCl₃, whereas the reactions with CF₃Cl and CF₃Br are reported to be slower than the collision rate.^{9,10} Under our experimental conditions, the O^{-•} ion also reacts readily with nearly all the selected halomethanes, as indicated by the finding that more than 90% of the reactant ions have been converted into products at a reaction time of 0.4 s. In line with the reported studies, this conversion into products at a reaction time of 0.4 s is lower for the CF₃Cl and CF₃Br species; that is, 55% for CF₃Cl and 75% for CF₃Br as the substrate (see also Fig. 1). Notwithstanding that a determination of the rate constants for the overall processes was not attempted, the ready conversion into products indicates that the O^{-•} ion also reacts with nearly all the halomethanes examined at a rate close or equal to the collision rate under the present experimental conditions.

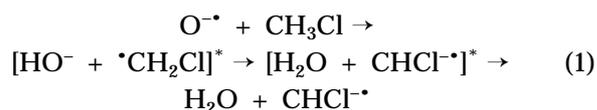
In the present study, the main concern is a determination of the relative yields of the various product ions formed under low pressure conditions, free from

contributions from reactions of species other than the O^{-•} ion. These product-ion distributions are collected in Table 1 for the chloro- and bromomethanes, whereas the results for chlorofluoro- and bromofluoromethanes are given in Table 2.

The product ion distributions given in Tables 1 and 2 refer mostly to a reaction time of 0.1–0.2 s. In some instances the primary product ions appeared to react further with the parent halomethanes. For these systems, the initial relative yields of the product ions were determined by following the product ion distributions as a function of the reaction time. Subsequently, the normalized yields of the product ions were extrapolated graphically to zero reaction time, as described elsewhere.^{25,26}

Reactions with CH₃Cl and CH₃Br

The reaction of O^{-•} with chloromethane is reported to involve hydrogen atom abstraction with formation of HO⁻ ions, a nucleophilic substitution process yielding Cl⁻ ions, and a formal H₂^{+•} abstraction leading to CHCl^{-•} radical anions.^{2,5,8,11} The latter reaction is considered to proceed by an initial hydrogen-atom abstraction forming a complex of a HO⁻ ion and a CH₂Cl^{-•} radical which reacts further by proton abstraction as indicated in Reaction (1).



The three processes are all estimated to be exothermic and compete efficiently with each other (Table 1).^{11,27,28} At a partial pressure of nitrous oxide of 3×10^{-6} Pa in the FTICR cell, the relative yields of the HO⁻, Cl⁻ and CHCl^{-•} product ions are 45%, 30% and 25%, respectively, whereas the relative yields of these ions are 25%, 30% and 45% if the partial pressure of nitrous oxide is 3×10^{-4} Pa. In other words, at a relatively low pressure of nitrous oxide in the FTICR cell, the reaction leading to HO⁻ dominates, whereas at a higher pressure of nitrous oxide, the formation of the CHCl^{-•} radical anions is relatively more important than the other reactions. In qualitative terms, this may be related to the formation of the O^{-•} ions by dissociative electron capture by nitrous oxide. As often emphasized

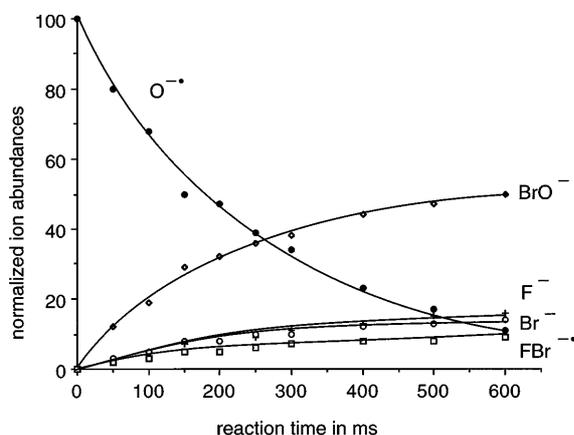


Figure 1. Variation in the normalized ion abundances as a function of time for the reaction of O^{-•} with CF₃Br; $p(\text{N}_2\text{O}) \approx 3 \times 10^{-6}$ Pa and $p(\text{CF}_3\text{Br}) \approx 3 \times 10^{-5}$ Pa.

Table 1. Normalized abundances (in %) of the product ions formed in reactions of the O^{-•} ion with chloro- and bromomethanes together with the estimated reaction enthalpies^a

Halomethane	Product ions	Possible neutral products	X = Cl		ΔH_i^d (kJ mol ⁻¹)	X = Br		ΔH_i^d (kJ mol ⁻¹)
			1 ^b	2 ^c		1 ^b	2 ^c	
CH ₃ X	HO ⁻	CH ₂ X [•]	45	25	-43	10	10	-37
	X ⁻	CH ₂ O [•]	30	30	-238	55	35	-268
	CHX ⁻	H ₂ O	25	45	-68	25	55	-79
	CH ₂ X ⁻	HO [•]			58	10		44
CH ₂ X ₂	HO ⁻	CHX ₂ [•]	15		-56			-63
	X ⁻	CH ₂ X [•] +O ^e	30		130	35	45	94
		CHX+HO ^f			117			87
		CH ₂ +XO ^g			252			191
		CH ₂ XO ^h						
		CH ₂ O+X ⁱ			-227			-322
	XO ⁻	CH ₂ X [•]			-10	15	10	-43
	CX ₂ ⁻	H ₂ O	25		-191	15	15	-236
	CHX ₂ ⁻	HO [•]	30		-32	35	30	-45
	CHX ₃	X ⁻	CHX ₂ [•] +O ^e	35	20	112	25	25
		CX ₂ +HO ^f			27			-5
		CHX+XO ^g			188			154
		CHX ₂ O ^h						
		CHXO+X ⁱ			-275			-344
XO ⁻		CHX ₂ [•]	25	25	-28	30	25	-47
X ₂ ⁻		CHXO	≈ 1	3	-400	5	5	-485
CX ₂ ⁻		HOX	≈ 1	2	-20	10	10	-94
CX ₃ ⁻		HO [•]	38	50	-105	30	35	-135
CX ₄		X ⁻	CX ₃ [•] +O ^e	30		90	60	30
		CX ₂ +XO ^g			82			22
		CX ₂ O ^h						
		CX ₂ O+X ⁱ			-339			-406
	XO ⁻	CX ₃ [•]	38		-40	10	20	-88
	X ₂ ⁻	CX ₂ O	≈ 2		-465			-546
	CX ₂ ⁻	X ₂ O					5	
	CX ₃ ⁻	XO [•]	30		-50	20	35	-108
	CX ₄ ⁻	O				10	10	

^a See also text.^b Partial pressure of N₂O ≈ 3 × 10⁻⁵ Pa.^c Partial pressure of N₂O ≈ 3 × 10⁻⁴ Pa (see 'Experimental').^d The reaction enthalpies refer to a temperature of 298 K and were estimated on the basis of data given in Refs. 11, 27, 28, 31 and 32.^e Dissociative electron transfer.^f α-elimination.^g Attack on a halogen atom followed by dissociation of the initially formed halogen-containing methyl anion.^h S_N2 substitution.ⁱ S_N2 substitution followed by dissociation of the initially generated halogen-containing methoxy radical.

in the literature,² this process leads to O^{-•} ions with a distribution of kinetic energies centered around a value of 0.4 eV if the electron energy is ≈ 1.2 eV.²⁹ Under the present experimental conditions, the kinetic energy distribution of the O^{-•} ions can be shifted to lower values by non-reactive collisions with nitrous oxide and by the known oxygen atom interchange with this substrate.^{21,22,30} This implies that, at the relatively low pressures of nitrous oxide, the fraction of the O^{-•} ions with a relatively high kinetic energy can be larger than at a relatively high nitrous oxide pressure in the FTICR cell. With respect to the reaction with chloromethane, more collision complexes will be generated with a relatively high internal energy at a low N₂O pressure than at a higher pressure. As a result, a relatively large fraction of the [HO⁻ + [•]CH₂Cl] complexes (see Reaction (1)) generated at a low partial pressure of nitrous oxide may tend to dissociate to afford HO⁻ ions instead of reacting further by proton transfer to yield the carbene radical anions. In other words, hydrogen-atom abstraction leading to free HO⁻ ions may be favoured over the multistep process leading to the carbene

radical anions at relatively high internal energies of the collision complexes.

The presently measured relative yields of the product ions of the reaction between O^{-•} and CH₃Cl lie between the values obtained with the high pressure FA and SIFT methods; in an FA study, the relative yields of the HO⁻, Cl⁻ and CHCl⁻ ions are given as 15%, 19% and 66%, respectively,⁸ whereas a SIFT study indicates that these ions are generated in relative yields of 45%, 40% and 15%.¹⁰ Notwithstanding that the pronounced formation of the CHCl⁻ ions in the former study is in line with the suggestion that this process may be favoured at thermal energies of the O^{-•} ion, the latter study indicates a preference for the formation of HO⁻ ions, as reported earlier for the reactions of quasi-thermal O^{-•} ions in a tandem mass spectrometer (53% HO⁻, 10% Cl⁻ and 37% CHCl⁻).⁴

The results in Table 1 indicate that the O^{-•} ion reacts similarly with CH₃Br as with CH₃Cl. At a relatively low pressure of N₂O, the Br⁻ ions are formed preferentially, whereas the reaction leading to CHBr⁻ dominates if the nitrous oxide pressure is increased.¹¹ In addition, at

Table 2. Normalized abundances (in %) of the product ions formed in reactions of the O⁻ ion with chlorofluoro- and bromofluoromethanes^a

Halomethane	Product ions	Possible neutral products	X = Cl ^b	ΔH_f° (kJ mol ⁻¹)	X = Br		ΔH_f° (kJ mol ⁻¹)
					1 ^b	2 ^d	
CF ₃ X	F ⁻	CF ₂ XO [•]	45		15	20	
		CF ₂ O+X ^c		-166			-236
	X ⁻	CF ₃ +O ^e	35	164	15	15	117
		CF ₃ O ^f		-267			-314
		CF ₂ O+F ^g		-185			-232
	XO ⁻	CF ₃ [•]	5	24	60	50	-20
FX ⁻	CF ₂ O	15	-233	10	15		
CF ₂ X ₂	X ⁻	CF ₂ X+O ^c	48	115	55	60	
		CF ₂ +XO ^h		72			15
		CF ₂ XO ^f					
		CF ₂ O+X ^g		-377			-470
	XO ⁻	CF ₂ X [•]	25	-25	15	10	
	X ₂ O ⁻	CF ₂	25		20	20	
	X ₂ ⁻	CF ₂ O	≈ 2	-503			
	CF ₂ X ⁻	XO [•]			10	10	
CFX ₃	X ⁻	CFX ₂ +O ^c	25	109	40		
		CFX+XO ^h		54			
		CFX ₂ O ^f					
		CFXO+X ^g		-375			
	XO ⁻	CFX ₂ [•]	40	-31	10		
	X ₂ O ⁻	CFX			10		
	X ₂ ⁻	CFXO		-500			
	CFX ₂ ⁻	XO [•]	35		40		

^a See also text.^b Partial pressure of N₂O ≈ 3 × 10⁻⁵ Pa.^c The reaction enthalpies were estimated on the basis of data given in Refs. 27, 31 and 32 and refer to a temperature of 298 K.^d Partial pressure of N₂O ≈ 3 × 10⁻⁵ Pa.^e Dissociative electron transfer.^f S_N2 substitution.^g S_N2 substitution followed by dissociation of the initially generated halogen-containing methoxy radical.^h Attack on a halogen atom followed by dissociation of the initially formed halogen-containing methyl anion.

low pressures of nitrous oxide in the FTICR cell, proton transfer with formation of CH₂Br⁻ ions is observed to a minor extent. This process is estimated to be endothermic²⁷ by ≈ 44 kJ mol⁻¹ and its occurrence is in keeping with the suggestion that, in the experiments performed with a relatively low pressure of nitrous oxide, a certain fraction of the O⁻ ions retains a kinetic energy greater than thermal. Even though the overall rate constant for the reaction of the O⁻ ion with CH₃Br has been measured with the FA method,⁵ the initial relative yields of the HO⁻, Br⁻ and CHBr⁻ ions were not reported. It was noted, however, that the formation of Br⁻ ion was enhanced relative to the formation of Cl⁻ ions in the reaction with CH₃Cl. In an early series of experiments performed with tandem mass spectrometry,⁴ the relative yields of the product ions of the reaction with CH₃Br were given as 52% HO⁻, 14% Br⁻ and 33% CHBr⁻ ions, indicating a preference for the formation of HO⁻ ions. This is in contrast with the present series of experiments which indicates that hydrogen-atom abstraction is a minor pathway.

Reactions with CH₂Cl₂ and CH₂Br₂

The O⁻ ion reacts with CH₂Cl₂ to afford HO⁻, Cl⁻, CCl₂⁻ and CHCl₂⁻ ions in relative yields of 15%, 30%, 25% and 30%, respectively, at a nitrous oxide pressure of 3 × 10⁻⁶ Pa in the FTICR cell. The formation of HO⁻ by hydrogen-atom abstraction, the formal H₂⁺ abstraction leading to the CCl₂⁻ ion as well as the proton transfer reaction are all estimated to be exo-

thermic (Table 1).^{27,28,31} A similar situation is likely to apply to formation of Cl⁻ ions by a nucleophilic substitution process, even though the absence of an enthalpy of formation of the assigned neutral product, ClCH₂O[•], prevents an estimation of this quantity. The product-ion distribution of the reaction of O⁻ with CH₂Cl₂ has been determined by the FA method to be 6% HO⁻, 13% Cl⁻, 55% CCl₂⁻ and 26% CHCl₂⁻ ions.⁸ With the exception of the relative yield of HO⁻ ions, similar results have been obtained by the SIFT method; that is, 18% Cl⁻, 55% CCl₂⁻ and 25% CHCl₂⁻ ions together with minor amounts of ClO⁻ and Cl₂⁻ ions.¹⁰ The main difference between these findings and the present FTICR results is a more-pronounced formation of the CCl₂⁻ ions in the FA and SIFT experiments and a lower abundance of HO⁻ ions. In keeping with the considerations for the reaction with CH₃Cl, the relatively lower yield of the CCl₂⁻ ions in the FTICR experiments can be related to the presence of O⁻ ions with a kinetic energy greater than thermal and the expected tendency of these O⁻ ions to form [HO⁻ + CHCl₂[•]] complexes which prefer to dissociate with formation of HO⁻ ions.

The O⁻ ion also reacts with CH₂Br₂ by competing proton transfer and H₂⁺ abstraction leading to CBr₂⁻ radical anions (Table 1). Hydrogen-atom abstraction is not observed, even though this process is estimated to be exothermic by 63 kJ mol⁻¹.^{27,28} In contrast to the results for CH₂Cl₂, attack on a halogen atom (Reaction (2)) is a dominant and relatively exothermic process for CH₂Br₂.



For this halomethane, the only difference between the product-ion distributions obtained at the different pressures of nitrous oxide in the cell is a somewhat more-pronounced tendency to form Br⁻ ions at a relatively high pressure of N₂O.

Reactions with CHCl₃ and CHBr₃

Proton transfer is the main process in the reactions of O^{-•} with CHCl₃ (Table 1) in agreement with the fact that this halomethane is much more acidic than the HO[•] radical in the gas phase.²⁷ Formation of Cl⁻ ions and attack on a chlorine atom with formation of ClO⁻ ions are the other major processes, whereas only traces of Cl₂^{-•} ions and also CCl₂^{-•} ions are formed, in particular at a relatively high pressure of nitrous oxide in the FTICR cell. Similar findings are reported for the reactions of the O^{-•} ion with CHCl₃ in a SIFT instrument; that is, 30% Cl⁻, 20% ClO⁻ and 48% CCl₃⁻ ions are formed at the relatively high pressure in such an instrument.¹⁰ In addition, minor amounts (2%) of Cl₂^{-•} ions were formed in the SIFT experiments, whereas CCl₂^{-•} ions were not observed. The reaction of the O^{-•} ion with CHBr₃ also involves mainly proton transfer, formation of BrO⁻ ions by attack on a bromine atom and the generation of bromide ions. In addition CBr₂^{-•} radical anions are formed in a relative yield of 10% together with traces of Br₂^{-•} ions. The results given in Table 1 indicate that the yields of the various product ions are not significantly affected by the pressure of nitrous oxide in the FTICR cell.

Reactions with CCl₄ and CBr₄

Attack on a chlorine atom in CCl₄ by the O^{-•} ion is likely to lead to ClO⁻ as well as CCl₃⁻ ions, in keeping with the fact that the formation of both ions by such a pathway is estimated to be exothermic (Table 1).²⁷ Somewhat more Cl⁻ ions (30%) are generated in the present experiments as compared to the number in a SIFT study of the reaction with CCl₄ (15% Cl⁻, 45% ClO⁻ and 35% CCl₃⁻ ions).¹⁰ With both methods, however, minor amounts (2–5%) of Cl₂^{-•} ions arise in the reaction of O^{-•} with CCl₄. With CBr₄ as the substrate, minor amounts of stable CBr₄^{-•} radical anions are generated in addition to Br⁻ ions and the expected product ions of bromine-atom attack, BrO⁻ and CBr₃⁻ (Table 1). The formation of Br⁻ ions is more pronounced at a low pressure of nitrous oxide than at a relatively high pressure of this species in the FTICR cell as indicated in Table 1. This may reflect, as mentioned previously, that at a low pressure of nitrous oxide, a certain fraction of the O^{-•} ions has a kinetic energy greater than thermal (*vide supra*). As a result, relatively more Br⁻ ions may arise by slightly endothermic processes such as initial attack on a bromine atom, with formation of CBr₃⁻ ions which may dissociate into CBr₂ and Br⁻ (Reaction (3); $\Delta H_f^\circ = 22 \text{ kJ mol}^{-1}$; see further 'Discussion').^{27,32}



Reactions with CF₃Cl and CF₃Br

The O^{-•} ion reacts with CF₃Cl to afford F⁻, Cl⁻, ClO⁻ and FCl^{-•} ions in relative yields of 45%, 35%, 5% and

15%, respectively, under the present experimental conditions (Table 2). In the SIFT study by Mayhew *et al.* of the reactions of thermal O^{-•} ions with CF₃Cl, the F⁻, Cl⁻ and FCl^{-•} ions were observed to be formed in relative yields of 50%, 30% and 20%,¹⁰ whereas in a study by Morris, the relative yields of these three product ions were determined to be 64%, 19% and 17% at a temperature of 300 K.⁹ At a temperature of 500 K, however, the normalized yields changed to 54% F⁻, 21% Cl⁻ and 23% FCl^{-•} ions.⁹ In addition, at a temperature of 500 K minor amounts (2%) of ClO⁻ ions were also generated. The generation of the ClO⁻ ions at a temperature of 500 K is in line with the present FTICR results of the reaction between the non-thermalized O^{-•} ions and CF₃Cl.

Similar results are obtained for the reactions of the O^{-•} ion with CF₃Br; that is F⁻, Br⁻, BrO⁻ and FBr^{-•} ions are generated (Table 2). The formation of BrO⁻ ions by bromine atom attack is estimated to be exothermic by 20 kJ mol⁻¹ for this system, and appears to be the main reaction. At a relatively low pressure of nitrous oxide in the cell, the BrO⁻ ions are formed in a relative yield of 60%, whereas the yield of these product ions is somewhat lower (50%) at the higher nitrous oxide pressure (see Table 2 and Fig. 1). Similarly, in the SIFT study by Morris, the product ion distribution is given as 45% F⁻, 8% Br⁻, 34% BrO⁻ and 13% FBr^{-•} ions at a temperature of 300 K and as 34% F⁻, 11% Br⁻, 48% BrO⁻ and 8% FBr^{-•} ions at a temperature of 500 K.⁹ As noted for the reactions with CF₃Cl, attack on the heavy halogen atom appears to be more pronounced for the non-thermalized O^{-•} ions in the FTICR experiments and at a temperature of 500 K in the SIFT instrument.

Reactions with CF₂Cl₂ and CF₂Br₂

In the reactions with CF₂Cl₂, traces of Cl₂^{-•} ions are generated, as indicated in Table 2. The main products are Cl⁻, ClO⁻ and Cl₂O^{-•} ions and in addition traces of CF₂Cl⁻ ions are formed. With the exception of the relative abundance of the Cl₂^{-•} ions, the present yields of the main product ions (Table 2) are in line with results obtained by the SIFT method; that is, in such an instrument the Cl⁻, ClO⁻, Cl₂O^{-•} and Cl₂^{-•} ions are formed in relative yields of 50%, 15%, 20% and 10%, respectively.¹⁰ With CF₂Br₂, the O^{-•} ion reacts to afford Br⁻, BrO⁻, Br₂O^{-•} and CF₂Br⁻ in relative yields which are generally similar at the different pressures of nitrous oxide in the FTICR cell (Table 2).

Reactions with CFCl₃ and CFBr₃

The formation of the ClO⁻ and CFCl₂⁻ ions in the reactions with CFCl₃ can be ascribed to attack on a chlorine atom. In contrast to the findings for CF₂Cl₂, no Cl₂O^{-•} ions are formed in the reactions with CFCl₃. In comparison with the reported results of experiments performed using the SIFT method (35% Cl⁻, 30% ClO⁻, 5% Cl₂^{-•} and 30% CFCl₂⁻),¹⁰ a somewhat higher yield of the ClO⁻ ions and a lower yield of Cl⁻ ions are obtained in the present FTICR experiments (see Table 2). In addition, we observed only traces of the Cl₂^{-•} ions which are reported to be formed in a relative yield of 5% in the SIFT experiments. With CFBr₃ as the substrate, Br₂O^{-•} ions are generated, as observed also for the reactions with the CF₂Br₂. In line with the results for CFCl₃ CFBr₂⁻ ions are formed in a relatively

Table 3. Normalized abundances (in %) of product ions formed in the reactions of the O⁻ radical anion with dibromodichloromethane and dibromochlorofluoromethane^a

Halomethane	Product ions	Possible neutral products	X = Cl	X = F
CXClBr ₂	Cl ⁻	CXBr ₂ O [•]	10	5
	ClO ⁻	CXBr ₂ ⁻	5	5
	Br ⁻	CXCIBrO [•]	45	45
	BrO ⁻	CXCIBr ⁻	15	15
	Br ₂ O ⁻	CXCl		5
	CFCIBr ⁻	BrO [•]		15
	CCl ₂ Br ⁻	BrO [•]	10	
	CFBr ₂ ⁻	ClO [•]		10
	CClBr ₂ ⁻	ClO [•]	15	

^a See also text. The experiments were performed with a partial pressure of N₂O of $\approx 3 \times 10^{-5}$ Pa (see also 'Experimental').

large yield indicating that attack on a bromine atom may result preferentially in this ionic species and to a lesser extent in BrO⁻ and Br₂O⁻ ions (Table 2).

Reactions with CCl₂Br₂ and CFCIBr₂

With the substrate, CCl₂Br₂, a series of product ions are formed as a result of competing attack on a chlorine and a bromine atom (Table 3). The occurrence of attack on a chlorine atom is evidenced by the generation of the ClO⁻ and CClBr₂⁻ ions, whereas attack on a bromine atom is indicated by the formation of the BrO⁻ and CCl₂Br⁻ ions (Table 3). Similar findings apply to CFCIBr₂ with the exception that Br₂O⁻ ions arise as a consequence of attack on a bromine atom by the O⁻ ion.

DISCUSSION

The present series of results extends the previous findings for the reactions of the atomic oxygen radical anion with halomethanes occurring at relatively high pressures.⁵⁻¹⁰ Most of the present results for the low-pressure reactions with the chloromethanes and chlorofluoromethanes are either in agreement with the reported FA and SIFT measurements or the differences can be understood in terms of the presence of O⁻ ions with a kinetic energy greater than thermal in our FTICR experiments. Moreover, the present results for the reactions of the O⁻ ion with the chloro- and bromomethanes provide a more complete picture of the relative importance of processes such as electron transfer, proton transfer, hydrogen-atom abstraction, formal H₂⁺ abstraction and attack on either the carbon atom or at a halogen atom. For the chloro- and bromofluoromethanes, the results reveal that the O⁻ ion reacts largely by competing attack on the carbon atom and a chlorine or bromine atom, whereas no evidence is obtained for the occurrence of initial attack on a fluorine atom.

Electron transfer

Electron transfer with formation of stable halomethane radical anions occurs only in the reaction with CBr₄ (Table 1) indicating that the electron affinity of this halomethane is larger than that of the oxygen atom (Electron affinity (EA) = 141 kJ mol⁻¹).²⁷ The absence of electron transfer in the reactions with CHCl₃ is in

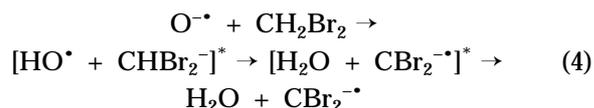
agreement with our recent finding that the electron affinity of CHCl₃ is between 45 and 75 kJ mol⁻¹.²⁵ Likewise, the non-occurrence of electron transfer with the formation of CCl₄⁻ ions is in keeping with our previous observation that the electron affinity of CCl₄ is between 45 and 110 kJ mol⁻¹.²⁵

Formation of molecular radical anions of the chloro- and bromofluoromethanes is not observed (Tables 2 and 3). For the chlorofluoromethanes as well as for the CF₃Br species, this is in line with the fact that the electron affinities are lower than of the oxygen atom (EA(CF₃Cl)³³ < 40 kJ mol⁻¹, EA(CF₂Cl₂)²⁷ \approx 40 kJ mol⁻¹, EA(CFCl₃)²⁵ \leq 98 kJ mol⁻¹ and EA(CF₃Br)²⁷ \approx 95 kJ mol⁻¹). For the substrates, CF₂Br₂, CFCIBr₃, CCl₂Br₂ and CFCIBr₂, no electron affinities are reported, thus precluding a conclusion as to whether electron transfer is thermodynamically unfavoured or unable to compete kinetically with other processes.

H⁺, H[•] and H₂⁺ abstractions

Proton transfer is, as expected, an important pathway if the reaction is exothermic and, for the CH₃Br substrate, is also observed in the reactions of O⁻ ions with a kinetic energy greater than thermal (see 'Results'). Hydrogen-atom abstraction with formation of HO⁻ ions is observed only for CH₃Cl, CH₃Br and CH₂Cl₂, even though it is exothermic for all halomethanes containing hydrogen atoms (see Table 1; $\Delta H_f^\ddagger = -61$ kJ mol⁻¹ for CHCl₃ and -64 kJ mol⁻¹ for CHBr₃).^{27,28,32} In this respect, the absence of hydrogen-atom abstraction in the reaction with CHCl₃ and CHBr₃ indicates that this pathway is unable to compete with a significantly exothermic proton transfer.

H₂⁺ abstraction is a major process in the reactions with CH₃Cl, CH₃Br, CH₂Cl₂ and CH₂Br₂ (Table 1). As indicated in Reaction (1), this process is likely to proceed by initial hydrogen-atom abstraction followed by proton abstraction for the substrates CH₃Cl and CH₃Br. This is in keeping with the fact that initial hydrogen-atom abstraction is exothermic overall, whereas an initial proton abstraction is endothermic for both substrates. Moreover, the CH₂Cl[•] and CH₂Br[•] radicals present in the ion/molecule complexes formed by the initial hydrogen-atom abstraction are known to be more acidic than water in the gas phase.¹¹ For CH₂Cl₂ and CH₂Br₂, the situation is less clear, since an initial hydrogen-atom abstraction, as well as an initial proton transfer, is exothermic overall as indicated in Table 1.^{27,32} This implies that the CCl₂⁻ or CBr₂⁻ radical anions can arise by initial proton transfer followed by hydrogen-atom abstraction as shown in Reaction (4) for the reaction with CH₂Br₂.



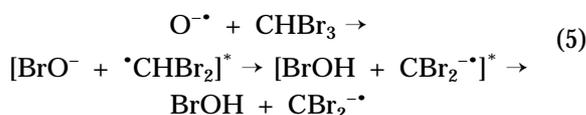
Overall, the second step in this sequence is estimated to be exothermic by 160 kJ mol⁻¹ for the CHCl₂⁻ ion and by 190 kJ mol⁻¹ for the CHBr₂⁻ species.^{27,32}

Attack on a halogen atom

Direct attack on a halogen atom in an organic compound by a negative ion has been described for reactions occurring in the condensed phase^{34,35} and

recently for the gas-phase reactions of various (radical) anions with halomethanes.^{26,36} Based on the results for the gas-phase reactions of (radical) anions other than the O^{-•} ion, it has been concluded that attack on a halogen atom becomes more pronounced as the number of halogen atoms is increased and that this process is less facile for chlorine- than for bromine-containing species. With respect to the O^{-•} ion, attack on a chlorine atom in chloromethanes and chlorofluoromethanes has been reported,¹⁰ whereas the relative importance of this pathway in the reactions with bromine-containing methanes other than CF₃Br has not been examined.⁹

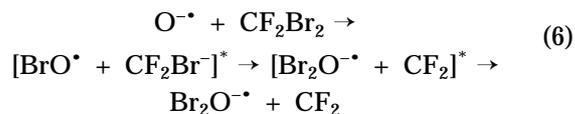
For the present systems, the attack on a chlorine atom with formation of ClO⁻ ions is a pronounced process for CHCl₃ and CCl₄. The reactions of O^{-•} with these substrates may thus serve as experimental entries to a study of the bimolecular reactivity of the ClO⁻ ion, which has been examined recently by dynamic and electronic calculations.³⁷ With respect to the experiments with CCl₄, chlorine atom attack by the O^{-•} ion can also be held responsible for the generation of the CCl₃^{-•} ion, indicating that ≈ 70% of all product ions arise by this pathway (Table 1). For the bromomethanes, the occurrence of attack on a halogen atom is revealed by the formation of BrO⁻ ions and for CBr₄ also by the generation of CBr₃^{-•} ions. In addition, attack on a bromine atom may also be involved in the process leading to the CBr₂^{-•} ions which are formed in a relatively low yield in the reactions with CHBr₃ and CBr₄. If initial attack on a bromine atom in, for example, CHBr₃ occurs this will give rise to a complex of a BrO⁻ ion and a CHBr₂[•] radical, which can react further by proton transfer prior to dissociation with formation of CBr₂^{-•} (Reaction (5)).



The initial attack on a bromine atom with formation of BrO⁻ ions is exothermic overall by 47 kJ mol⁻¹ for the reaction with CHBr₃.^{27,28,32} The second step in the reaction sequence (5) is also predicted to be exothermic overall, in keeping with the fact that the CHBr₂[•] radical is determined to have a gas-phase acidity of ΔH^o_{acid} = 1469 ± 5 kJ mol⁻¹,³² whereas the value for BrOH is estimated to be ≈ 1510 kJ mol⁻¹.²⁷ Alternatively, the first step in the reaction with CHBr₃ could be a hydrogen-atom abstraction with formation of a [HO⁻ + CBr₃[•]]^{*} complex, which then reacts further by halogen attack and dissociation. Irrespective of the precise mechanism, the overall reaction leading to the CBr₂^{-•} ions is estimated to be exothermic by 94 kJ mol⁻¹ (Table 1) on the basis of thermochemical data for the parent CBr₂ carbene, as determined in a recent study by our group.³² For the formation of CBr₂^{-•} ions in the reaction with CBr₄, an estimate of the reaction enthalpy is hampered by the absence of thermochemical data for the expected neutral product, Br₂O.

With respect to the chlorofluoromethanes, attack on a chlorine atom yields ClO⁻ ions for all substrates. In addition, this process is likely to be responsible for the formation of the Cl₂O^{-•} ions if CF₂Cl₂ is the substrate and the CFCl₂^{-•} ions in the reaction with CFCl₃. Similarly, attack on a bromine atom yields only BrO⁻ in the reaction with CF₃Br, whereas this pathway leads to

Br₂O^{-•} ions as well as the halomethyl carbanions, CF₂Br^{-•} and CFBr₂^{-•}, in the reactions with CF₂Br₂ and CFBr₃, respectively. The reaction sequence (6) leading to Cl₂O^{-•} or Br₂O^{-•} ions may be formulated for the reaction with CF₂Br₂.



Initial attack on a bromine atom leads to a complex of a BrO[•] radical and a CF₂Br⁻ ion which may either dissociate to afford CF₂Br^{-•} ions or react by bromide-ion transfer. Alternatively, a complex of BrO⁻ and a CF₂Br[•] radical may arise initially and react further by attack on the bromine atom in the radical prior to dissociation with formation of Br₂O^{-•} ions.

In terms of the relative importance of halogen atom attack, the present results indicate that, in the reactions with the fully halogen substituted species, this pathway dominates the chemistry to a large extent. In line with the findings obtained for the reactions of (radical) anions and halomethanes,^{26,36} the O^{-•} ion also displays a somewhat greater tendency to attack a bromine atom than a chlorine atom. The tendency is not very pronounced, however, in the reactions with CCl₂Br₂ and CFCIBr₂ (Table 3). If the formation of halide ions is neglected (*vide infra*), the attack on a chlorine atom in CCl₂Br₂ with formation of ClO⁻ and CClBr₂[•] accounts for about 20% of the product ions, whereas bromine atom attack leading to formation of BrO⁻ and CCl₂Br⁻ ions accounts for 25% of the total yield of product ions. A similar conclusion is reached for the reactions with CFCIBr₂ if the statistical preference for attack on a bromine atom is taken into account as well as noting that this pathway also leads to Br₂O^{-•} ions in this system.

Pathways leading to halide ions

The formation of halide ions is, as expected, a common and dominant process in the reactions of O^{-•} with halomethanes. The mechanistic assignment of the process which may lead to these product ions is not straightforward, owing in part to the fact that the neutral products of these ion/molecule reactions are not detected and in part to the fact that various pathways may be energetically favourable, in particular in the reactions with the compounds containing three or four halogen atoms. As discussed for the reactions of various (radical) anions for halomethanes, the halide ions can arise by overall dissociative electron transfer, α-elimination, attack on a halogen atom and S_N2 substitution as summarized in Scheme 1.³⁶

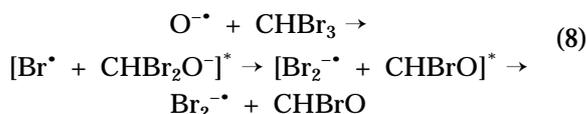
Dissociative electron transfer with formation of a halomethyl radical, an oxygen atom and a halide ion is indicated in Table 1 to be endothermic for the chloro- and bromomethanes. This process is associated with a favourable change in entropy which leads to a TΔS_r^o value of 34–44 kJ mol⁻¹ at a temperature of 298 K as discussed in a previous paper.³⁶ In terms of the change in Gibbs energy this indicates that dissociative electron transfer is only a feasible process for CBr₄ (ΔH_r^o = 49 kJ mol⁻¹ and ΔG_r^o ≈ 5 kJ mol⁻¹ at T = 298 K; Reaction (7)).^{27,28,32}



Similarly, dissociative electron transfer is unlikely to be an important pathway in the formation of halide ions in the reactions with chlorofluoro- and bromofluoromethanes, in keeping with the fact that this process is estimated to be significantly endothermic for most of the substrates (see Table 2). For CF₂Br₂, CBrF₃ as well as CCl₂Br₂ and CFCIBr₂, the thermochemical data available are too limited for an estimation of the enthalpy change for dissociative electron transfer. These considerations apply, of course, to thermal conditions and it cannot be excluded *a priori* that O^{-•} ions with an excess kinetic energy react by this pathway with some of the halomethanes.

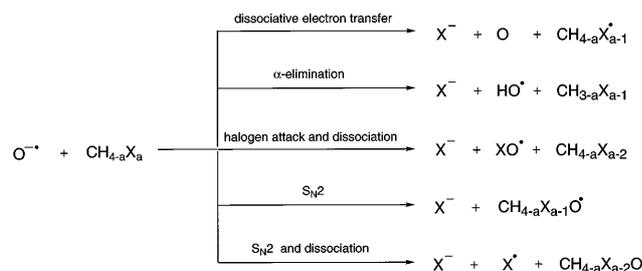
The α-elimination pathway is only energetically feasible for CHCl₃ and CHBr₃ as indicated in Table 1. With respect to the formation of halide ions by halogen attack followed by dissociation of the thus generated halomethyl carbanion (Scheme 1 and Reaction (4)), this reaction is only slightly endothermic for CBr₄ or CF₂Br₂ as the substrate and a similar situation may apply to CBrF₃ (Tables 1 and 2). In other words, the thermochemical considerations may suggest that halide ions are formed largely as a consequence of attack on the carbon atom. For the mono- and dihalogen substituted methanes this may be the only pathway for the formation of the halide ions, whereas the importance of other pathways is uncertain for the more fully substituted chloro- and bromomethanes. Nevertheless, the S_N2 substitution with formation of a halogen-containing methoxy radical is likely to be significantly exothermic for all halomethanes. This is supported by the finding that substitution followed by dissociation (Scheme 1) is estimated to be highly exothermic for the chloro- and bromomethanes (Table 1) and a similar situation applies to the fluorine-containing species (Table 2).

Attack on the carbon atom can also be responsible for the formation of the minor amounts of the Cl₂^{-•} ions generated in the reactions with CHCl₃ or CCl₄ and a similar proposal may apply to the formation of Br₂^{-•} if CHBr₃ is the substrate. The formation of these molecular, radical halogen anions by attack on the carbon atom could be formulated as shown in Reaction (8) for the reaction with CHBr₃.



In this reaction, the initial step results in a complex of a Br[•] atom and CHBr₂O^{-•} ion which then reacts by halide-ion transfer and dissociation to afford Br₂^{-•} ions and a CHBrO species (Reaction (8)). Such a mechanism may apply also to the formation of the FCl^{-•} and FBr^{-•} ions in the reactions with the CF₃Cl and CF₃Br species (Table 2) and the generation of the Cl₂^{-•} ions in the reaction with CF₂Cl₂.

Comparable considerations have been advanced previously for the generation of the Cl₂^{-•} ions in the reactions with tri- and tetrachloromethane and the FCl^{-•} ions in the reaction with CF₃Cl.¹⁰ In addition, a simplified mechanistic scheme was proposed in which all the Cl⁻ ions were indicated to arise by initial formation of Cl₂^{-•} ions with a distribution of internal energies. Subsequently, some of the Cl₂^{-•} or FCl^{-•} ions with a sufficient internal energy were considered to



Scheme 1. Possible pathways leading to the formation of halide ions in the reactions of O^{-•} with chloro- and bromomethanes (CH_{4-a}X_a; X = Cl and Br; a = 1–4).

dissociate with formation of the observed atomic halide ions.¹⁰ Even though such a mechanistic proposal may provide a relatively simple picture of the formation of halide ions, the present results suggest that it is not possible to exclude the occurrence of more than a single pathway in the overall process leading to the halide ions, in particular in the reactions with the tri- and tetra-halogen substituted methanes. In addition, a possible other source of the F⁻ ions in the reactions with the CF₃Cl and CF₃Br substrates could be substitution, with initial formation of a complex of a CF₃O^{-•} ion and halogen atom. This complex can then dissociate into F⁻, CF₂O and a halogen atom, thus leading to the same neutral products as indicated by initial formation of a FCl^{-•} ions and subsequent dissociation of some of these product ions.

CONCLUSIONS

The O^{-•} radical anion reacts readily in the gas phase with the halomethanes CH₃X, CH₂X₂, CHX₃, CX₄, CF₃X, CF₂X₂, CFX₃ (X = Br and Cl) and CXClBr₂ (X = Cl and F) with formation of a variety of product ions. For the chloro- and bromomethanes, the main pathways can be classified as H⁺ transfer, H[•] abstraction, H₂^{+•} abstraction, attack on a halogen atom and substitution by attack on the carbon atom. The trend in the product-ion distributions confirms that attack on a halogen atom is more likely for the bromomethanes than for the chloromethanes. The relative importance of attack on the carbon atom with formation of halide ions is less straightforward to establish for the chloro- and bromomethanes with more than two halogen atoms, since the halide ions can arise by other pathways, such as α-elimination or halogen attack followed by dissociation of the initially generated product ions. Likewise, for the chlorofluoro- and bromofluoromethanes, the main reactions are attack on a chlorine or bromine atom and reaction at the carbon atom. Halogen-atom attack appears to be an important pathway for the fluorine-containing halomethanes and is likely to lead to the relatively abundant Cl₂O^{-•} and Br₂O^{-•} ions formed in the reactions with CF₂Cl₂ and CF₂Br₂, respectively. In addition, the halide ions formed in the reactions with the chlorofluoro- and bromofluoromethanes may arise largely as a result of attack on the carbon atom, notwithstanding that other processes, such a halogen attack followed by dissociation of the initially formed product ion, may also play a role in the reactions with the CF₂Br₂ and CBrF₃ species. Stated differently, the uncertainty in the nature of the process(es) leading to the abundant halide ions prevents a simplified mechanistic picture being

advanced for the reactions with all the different halomethanes included in this study.

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