Reaction of F Atoms with Methyl Nitrite. Infrared Spectroscopic Evidence for the Stabilization of FON in an Argon Matrix

Marilyn E. Jacox

Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234 *(Received: January 18, 1983)*

When the products of the reaction between F atoms formed in a microwave discharge and methyl or methyl-d_3 nitrite are frozen in a large excess of argon at 14 K, prominent absorptions of FNO appear in the infrared spectrum of the solid deposit, demonstrating that NO abstraction occurs. Two absorptions previously attributed to FON are also very prominent, supporting the identification of that isomer, but the assignment of the NO-stretching fundamental of FON was not confirmed. The appearance of infrared absorptions of isolated and hydrogen-bonded HF indicates that the more exothermic reaction channel involving H-atom abstraction also occurs. The absorptions of H_2CO and NO, products of the decomposition of CH_2ONO, are prominent, with indirect evidence that a small concentration of CH_2ONO may have been stabilized. Factors influencing the relative contributions of the two observed F-atom reaction channels are considered.

Introduction

Several aspects of the reaction of F atoms with methyl nitrite, which has not heretofore been studied, promise to be of interest in relation to theories of chemical bonding and reaction dynamics. The expected H-atom abstraction reaction

$$F + CH_3ONO \rightarrow CH_2ONO + HF \qquad (1a)$$

would be substantially exothermic. This process has been studied for a wide variety of hydrogen-containing molecules,[1-3] including the closely related species nitromethane.[4,5] Because methyl nitrite may be formed by the reaction of CH_3 with NO_2 in the upper atmosphere,[6,7] as well as in the thermal and photodecomposition of nitromethane,[8] and because a number of other atoms and small free radicals found in these same systems, including $O(^3P)$, OH, NH_2, CH_3, and CH_3O, also characteristically abstract H atoms, the possible formation of CH_2ONO in the F + CH_3ONO reaction would be of more general importance. Kinetic studies of the O + CH_3ONO reaction by Davidson and Thrush[9] indicate that CH_2ONO is formed in the primary reaction but that its decomposition by the reaction

$$CH_2ONO \rightarrow H_2CO + NO \qquad (1b)$$

occurs readily. Warneck and co-workers[10] also obtained evidence for the participation of a reaction channel involving CH_2ONO formation in the H + CH_3ONO reaction. If previously determined heats of formation[11,12] are used and Warneck's assumption of a C–H bond dissociation energy of 389 kJ/mol (93 kcal/mol) for CH_3ONO is adopted, reaction 1a would be exothermic by 179 kJ/mol (43 kcal/mol) and reaction 1b by 130 kJ/mol (31 kcal/mol). Therefore, as noted by Thrush, low-temperature studies would be required to determine whether CH_2ONO has a stable potential minimum.

The occurrence of the alternate reaction channel

$$F + CH_3ONO \rightarrow CH_3O + FNO \qquad (2)$$

estimated[11,12] to be exothermic by 65.7 kJ/mol (15.7 kcal/mol), would be of intrinsic interest. This reaction may also provide a suitable source of the important free radical CH_3O for spectroscopic study; other processes in which CH_3O is formed are complicated by secondary photodecomposition or by radical–radical reactions which efficiently remove CH_3O from the system.

In recent studies in this laboratory, a discharge F-atom source has been coupled with cryogenic sampling to study the reaction of F atoms with a number of molecules, including methane,[13] methyl fluoride,[14] methanol,[15a] acetaldehyde,[15b] and nitromethane.[5] In each of these systems, prominent infrared absorption of the free radical resulting from the primary H-atom abstraction reaction were identified. There was little evidence for secondary F-atom reactions and none for the reaction of NF or NF_2, also formed in the discharge, with other molecules in the system. The results of a similar study of the reaction of F atoms with methyl nitrite, undertaken to provide information on the mechanism of this reaction and on the stabilities and infrared spectra of the free radical products, are presented in the following discussion.

Experimental Details[16]

The procedure used for the synthesis and purification of methyl nitrite was similar to that reported by Sanders,[17] with the modifications described by Rook and Jacox[18] for

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[12] S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley, New York, 1976, pp 296, 299.

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[14] M. E. Jacox, *Chem. Phys.*, 59, 199 (1981).

[15] (a) M. E. Jacox, *Chem. Phys.*, 59, 213 (1981). (b) *Ibid.*, 69, 407 (1982).

[16] Certain commercial instruments and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

[17] N. Sanders, J. E. Butler, L. R. Pasternack, and J. R. McDonald, *Chem. Phys.*, 48, 203 (1980).

[18] F. L. Rook and M. E. Jacox, *J. Mol. Spectrosc.*, 93, 101 (1982).

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the synthesis of methyl-d_3 nitrite. The infrared spectra of the resulting samples showed no extraneous absorption. Ar:CH_3ONO and Ar:CD_3ONO samples of mole ratio 200 were prepared by using standard manometric procedures. The NO sample (Matheson Co., Inc.) used in supplementary experiments was freed of relatively volatile trace impurities by repeated freezing at 77 K and pumping on the solid sample. Ar:NO samples of mole ratio 200, 800, and 1600 were studied. The mole ratio of the Ar:NF_3 mixture used as the F-atom source was 200 in all of the experiments. Details of the preparation of the Ar:NF_3 samples and of the discharge configuration used to produce F atoms have previously been described.[13] The Ar:CH_3ONO-d_n sample was introduced into the low-temperature cell from a 2-L reservoir at a rate of approximately 10 torr/h, and the Ar:NF_3 sample was passed from a 2-L reservoir into the discharge region at a rate of approximately 7 torr/h. The pinhole in the end of the discharge tube serves both to maintain the pressure in the discharge region at approximately 1 torr and to prevent backstreaming of the CH_3ONO sample, introduced into the system just outside the pinhole, into the discharge region. The cryogenic equipment and the sample observation configuration have also previously been described.[19] All observations were conducted at 14 K.

After the infrared spectrum of the initial deposit had been recorded, the sample was subjected to the full or filtered radiation of a 140-W medium-pressure mercury arc, focused by a quartz lens, in order to determine the threshold and products of secondary photodecomposition. Corning filters of glass Type 0160 and 7740, with short wavelength cutoffs of 300 and 280 nm, respectively, were used in this series of experiments.

Infrared spectra were recorded with a Beckman IR-9 spectrophotometer. Under the scanning conditions typical of these experiments, the resolution and the relative and absolute frequency accuracies are estimated to be 1 cm^{-1} between 400 and 2000 cm^{-1} and 2 cm^{-1} between 2000 and 4000 cm^{-1}.

Observations

The positions and peak optical densities of all of the absorptions which are characteristic of the F + CH_3ONO reaction are summarized in the first two columns of Table I. In addition to these absorptions, prominent absorptions of unreacted CH_3ONO and of NF and NF_2, produced in the discharge, were present. The presence of trace atmospheric impurities in the discharge typically leads to the stabilization of small concentrations of FCO, F_2CO, OF_2, FO_2, FNO, and FNO_2 in such experiments.[13] The absorptions of the first four of these species (not included in Table I) were of no more than weak to moderate intensity, precluding the occurrence of a significant atmospheric leak in these experiments, but those of FNO were extremely strong, and the 1790-cm^{-1} absorption of FNO_2 was moderately strong. Since FNO must have been formed by the reaction of F atoms with CH_3ONO and such a reaction may have contributed to the formation of FNO_2, these absorptions are included in Table I. Peaks at 493 and 735 cm^{-1}, assigned by Smardzewski and Fox[20-22] to FON, were also extremely prominent, but the absorption at 1887 cm^{-1} which these workers found to be half as intense as the 493-cm^{-1} peak and which they also assigned to FON could have contributed only a weak, unresolved shoulder on the high-frequency side of the prominent 1875-cm^{-1} absorption. The appearance between 3880 and 4000 cm^{-1} of the three absorptions characteristic of HF isolated in solid argon[23] indicates that H-atom abstraction also occurs in this system. A pair of prominent absorptions at 3422 and 3432 cm^{-1} can tentatively be assigned to the HF-stretching vibration of HF hydrogen bonded to a reaction product, designated as species A. The very strong absorption at 1875 cm^{-1} may have been contributed by NO. However, the behavior of this absorption on photolysis of the sample adds some uncertainty to this assignment. The peaks at 1500 and 1741 cm^{-1} correspond to the two strongest absorptions of H_2CO isolated in solid argon.

TABLE I: Peak Optical Densities of CH_3ONO + F Reaction Product Absorptions in Initial Sample Deposit and After Mercury-Arc Irradiation

cm^{-1}	initial	$\lambda > 300$ nm	$\lambda > 250$ nm	assignment
493	0.387	0.237	0.118	FON
511	0.380	0.378	0.389	FNO
695	0.082	0.116	0.130	A···HF
735	0.467	0.373	0.239	FON
751	0.623	0.651	0.669	FNO
779	0.028	0.027	0.011	
1311	0.032	0.032	0.038	
1498		0.354	0.362	H_2CO···HNO
1500	0.081	sh	sh	H_2CO
1722	0.164	0.202	0.202	H_2CO···NO···HF
1734	0.021	0.645	0.620	H_2CO···HNO
1741	0.074	0.067	0.074	H_2CO
1790	0.082	0.084	0.092	FNO_2
1851	0.717	0.733	0.747	FNO
1863	0.275	0.282	0.190	FON ?
1875	0.434	0.287	sh	NO, FON ?
1879		sh	0.171	
3422	0.168	0.197	0.208	A···HF
3432	0.149	0.189	0.222	A···HF
3522	0.044	0.048	0.048	
3882	0.030	0.031	0.031	HF
3918	0.020	0.021	0.021	HF
3964	0.042	0.043	0.043	HF

Comparison of the relative intensities of the *cis*- and *trans*-CH_3ONO absorptions in F-atom reaction studies with those for simple deposits of CH_3ONO in an argon matrix[18,24] indicated that, within the experimental error, there was no evidence for selective reaction of F atoms with one of the two stable rotamers.

The threshold for the photodecomposition of CH_3ONO to produce H_2CO hydrogen bonded to HNO in the argon lattice lies near 370 nm,[24,25] whereas the photodecomposition threshold for the carrier of the peaks attributed to FON isolated in an argon matrix lies near 280 nm.[22] When the sample considered in Table I was exposed to mercury-arc radiation of wavelength longer than 300 nm for 97 min, the absorptions of *cis*-CH_3ONO were almost completely destroyed, those of *trans*-CH_3ONO were somewhat reduced in intensity, and prominent absorptions of hydrogen-bonded H_2CO···HNO molecular pairs appeared. These new absorptions, which were included in Table I only when they overlapped F-atom product absorptions, were unshifted from the positions previously reported.[24,25] The peak optical densities of the absorptions attributed to F-atom reaction products are summarized in the third column of Table I. Absorptions assigned to isolated HF

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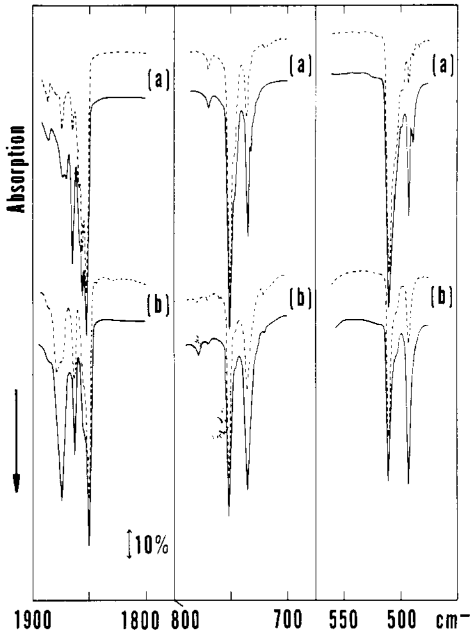

Figure 1. (a) — 4.39 mmol Ar:NO = 1600 codeposited over period of 267 min with 2.14 mmol discharged Ar:NF_3 = 200. ---- 108 min subsequent unfiltered mercury-arc photolysis. (b) — 2.35 mmol Ar:CH_3ONO = 200 codeposited over period of 145 min with 2.14 mmol discharged Ar:NF_3 = 200. ---- 97 min subsequent mercury-arc photolysis, λ > 300 nm, + 25 min unfiltered mercury-arc photolysis.

and H_2CO and to FNO and FNO_2 were unchanged in intensity. The peaks attributed to FON at 493 and 735 cm^{-1} diminished significantly in intensity, as did the very strong peak at 1875 cm^{-1}, which was broadened by the appearance of a high-frequency shoulder. The absorptions at 695, 1722, 3422, and 3432 cm^{-1} grew somewhat.

After this sample had been exposed to the full light of the medium-pressure mercury arc for 25 min, the absorptions of *trans*-CH_3ONO were greatly diminished in intensity. The peak optical densities of absorptions characteristic of the presence of F atoms in the initial deposit are summarized in the fourth column of Table I. The intensities of the absorptions assigned to isolated HF, isolated and complexed H_2CO, FNO, and FNO_2 were invariant, whereas the FON peaks at 493 and 735 cm^{-1} diminished markedly in intensity. The 1863-cm^{-1} peak also diminished considerably, and the 1879-cm^{-1} peak was more intense than the remaining, partially resolved absorption at 1875 cm^{-1}. There may have been a small further growth in the intensities of the peaks at 695, 3422, and 3432 cm^{-1}.

Figure 1 contrasts the spectral regions of the FNO absorptions for an experiment in which F atoms reacted with a very dilute sample of NO with those for an F + CH_3ONO study. The NO concentration in the sample of Figure 1a was sufficiently low that the spectrum of the initial deposit (solid traces) showed only a moderately intense 1875-cm^{-1} absorption of unreacted NO and that the peak optical density of the 1778-cm^{-1} absorption of $(NO)_2$[26] was 0.01, implying that the contribution of $(NO)_2$ to the prominent 1864-cm^{-1} absorption was small. The three FNO absorptions were extremely strong, with some partially resolved structure. The 493- and 735-cm^{-1} peaks, which, as in the earlier work,[20-22] had low-frequency satellite absorptions, were prominent but were much less intense than the nearby FNO absorptions. The intensity of the 1887-cm^{-1} peak relative to the other two absorptions previously attributed to FON was much smaller than in the experiments of Smardzewski and Fox.[22] After the sample had been exposed to the full light of a medium-pressure mercury arc for 108 min, the spectra shown in the broken-line traces were recorded. Although the absorptions of FNO were unchanged, the absorptions at 493, 735, and 1864 cm^{-1} were greatly reduced in intensity, as was the 1873-cm^{-1} shoulder on the 1875-cm^{-1} absorption of NO. There was little change in the intensity of the 1887-cm^{-1} absorption. The traces of Figure 1b are portions of the spectra summarized in Table I. The positions of the major absorptions correspond within the experimental error with those of Figure 1a, although somewhat less structure is resolved. However, in the F + CH_3ONO experiment the intensities of the 493- and 735-cm^{-1} absorptions are almost as great as those of the nearby FNO absorptions.

TABLE II: Peak Optical Densities of CD_3ONO + F Reaction Product Absorptions in Initial Sample Deposit and After Mercury-Arc Irradiation

cm^{-1}	initial	λ > 280 nm	λ > 250 nm	assignment
419	0.029	0.029	0.023	
463	0.025	0.030	0.035	
493	0.778	0.808	0.076	FON
511	0.359	0.359	0.359	FNO
515			0.026	A···DF
721	0.018	0.018	0.000	
735	0.792	0.740	0.077	FON
751	0.500	0.500	0.477	FNO
814	0.019	0.028	0.041	FNO_2
967	0.015	0.015	0.015	
1000	0.000	0.000	0.051	
1310	0.024	0.024	0.024	
1578	0.037	0.045	0.037	
1678	0.017	0.017	0.127	D_2CO···NO···DF
1686	0.046	0.046	0.046	
1691	0.028	0.176	0.406	D_2CO···DNO
1699	0.034	0.033	0.045	D_2CO
1792	0.062	0.064	0.055	FNO_2
1852	0.541	0.539	0.557	FNO
1864	0.167	0.162	0.029	FON ?
1876	0.845	0.762	sh	NO, FON ?
1880	sh	sh	0.123	
2532	0.000	0.043	0.357	A···DF
2690	0.000		0.069	

The positions and peak optical densities of the absorptions which resulted from the reaction of F atoms with CD_3ONO isolated in an argon matrix are summarized in the first two columns of Table II. The FNO absorptions at 511, 751, and 1852 cm^{-1} were again very strong, but in this experiment the peaks at 493 and 735 cm^{-1} were significantly stronger than the nearby FNO absorptions. Within the experimental error, the peaks at 1864 and 1876 cm^{-1} were unshifted. There was no evidence for an absorption at 1887 cm^{-1}. No absorptions of isolated or hydrogen-bonded DF were present in the initial sample deposit, but relatively weak absorptions of isolated D_2CO and of D_2CO···DNO appeared.

After the sample had been exposed to mercury-arc radiation of wavelength longer than 280 nm for 50 min, the peak optical densities of the F-atom reaction products summarized in the third column of Table II were obtained. At this stage of the experiment, the intensities of the absorptions of *cis*-CD_3ONO were reduced by approximately 25%, while those of *trans*-CD_3ONO were slightly greater than in the initial deposit. The only other significant change in the spectrum was the growth in the absorptions previously assigned[24,25] to D_2CO···DNO.

After a 97-min period of irradiation by the full light of a medium-pressure mercury arc, the absorptions of both *cis*- and *trans*-CD_3ONO were almost completely destroyed

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[26] W. G. Fateley, H. A. Bent, and B. Crawford, Jr., *J. Chem. Phys.*, 31, 204 (1959).

and the absorptions of $D_2CO\cdots DNO$ were substantially more intense. The peak optical densities of the F-atom reaction product absorptions are summarized in the fourth column of Table II. Again, the FNO absorptions were invariant, the 493-, 511-, and 1864-cm^{-1} absorptions were greatly diminished in intensity, and the 1875-cm^{-1} peak was much less prominent, with an equally intense satellite at 1880 cm^{-1}. The 1678-cm^{-1} peak grew greatly in intensity, and a very prominent new peak appeared at 2532 cm^{-1}. Other new absorptions appeared at 515, 1000, and 2690 cm^{-1}.

In another experiment on the F + CD_3ONO reaction system, the 493- and 735-cm^{-1} absorptions were again considerably more prominent than the nearby FNO absorptions. This sample was exposed to 280-nm cutoff radiation for 127 min, resulting in almost complete destruction of the absorptions of *cis*-CD_3ONO and a large decrease in the intensities of the absorptions of *trans*-CD_3ONO. At this stage of the experiment, the peak optical densities of the 493-, 735-, and 1875-cm^{-1} absorptions were approximately halved, whereas that of the 1864-cm^{-1} absorption was almost unchanged. The absorption at 1678 cm^{-1} had become moderately strong and a prominent absorption at 2532 cm^{-1} had appeared.

Discussion

The existence of a potential minimum for FON was first suggested by the ab initio calculations of Peslak and coworkers.[27] The assignment of the infrared absorption spectrum of FON offered by Smardzewski and Fox[22] was followed by the ab initio calculations of Grein and coworkers,[28] which included configuration interaction and added polarization functions and which also yielded a potential minimum for FON. However, the isotopic shifts reported by Smardzewski and Fox for the 735-cm^{-1} absorption were, within an experimental error of 1 cm^{-1}, the same as those for the 751-cm^{-1} FNO absorption, and the isotopic shifts for the 493-cm^{-1} absorption were the same as those for the 511-cm^{-1} FNO absorption. The much higher frequency NO-stretching vibration is localized in the NO bond, and its isotopic shift pattern gives little information regarding the nature of other substituents in the molecule. Therefore, it is conceivable that the bands assigned to FON are in fact contributed by FNO trapped in a different type of site in the argon or nitrogen lattice. The unusually large site splittings (17 or 18 cm^{-1}) may have been a consequence of the significant ionic character of FNO.[28]

The appearance of prominent absorptions at 493 and 735 cm^{-1} in both the earlier studies of the F_2 + NO reaction and in the present studies of the F + CH_3ONO reaction supports their assignment to FON. The end oxygen atom of the methyl nitrite molecule would be expected to be more exposed to collisional interaction with a fluorine atom than would be the central oxygen atom. Furthermore, if FNO is extraordinarily sensitive to the nature of the trapping site in solid argon, the presence of CH_3O in a nearby site would be likely to give a different set of site perturbations from those characteristic of the F + NO system. The large differential between the photodecomposition thresholds of FNO and FON, observed in both studies, also supports the existence of both isomers.

The previous assignment of the 1887-cm^{-1} absorption to the NO-stretching vibration of FON is not confirmed by the present study. Many of the experiments of Smardzewski and Fox[20-22] were conducted at an Ar:NO or N_2:NO mole ratio of 250 and some at a mole ratio of 500. The isolation of NO in argon and nitrogen matrices is extraordinarily difficult, as is evidenced by the rather prominent absorptions of $(NO)_2$. The 1887-cm^{-1} absorption was also prominent in studies of the F + NO reaction in this laboratory in which more concentrated Ar:NO samples were used and the absorptions of $(NO)_2$ had significant intensities. Possibly the 1887-cm^{-1} absorption is contributed by a complex of F atoms or of F_2 with $(NO)_2$. The only other candidates for assignment to the NO-stretching fundamental of FON are the photolytically sensitive absorptions at 1864 and 1875 cm^{-1}, which would have been overlapped by much more prominent absorptions of NO and $(NO)_2$ in the earlier study. However, the peak optical densities of these absorptions are not in a sufficiently constant ratio to those of other FON absorptions for a positive assignment of either peak to FON. The ab initio calculations provide little guidance in predicting the position of this fundamental; Peslak and co-workers[27] calculated a longer NO bond for FON than for FNO, whereas Grein and co-workers[28] calculated the reverse relationship between the two bond lengths. Grein also predicted a highly ionic structure for FON, consistent with very strong infrared absorptions associated with the interionic modes (the OF-stretching and the bending fundamentals) and a comparatively weak absorption associated with the stretching of the covalent NO bond.

Despite the very prominent absorptions of FNO and FON, these experiments have yielded no spectral data for CH_3O. The CO-stretching fundamental of this species, assigned at 1015 cm^{-1} in the laser-excited fluorescence spectrum of CH_3O and at 1010 cm^{-1} in that of CD_3O,[29] was not observed in the scans of the spectra of the initial sample deposits, nor were there product absorptions of significant intensity in the spectral regions characteristic of CH-deformation and stretching modes. Possibly the infrared absorptions of CH_3O are inherently weak.

Although absorptions of FNO_2 usually contributed to the product spectra, they were only slightly more intense than in other F-atom reaction experiments, consistent with the estimation from tabulated heats of formation[11,12] that the reaction

$$F + CH_3ONO \rightarrow CH_3 + FNO_2 \qquad (3)$$

is endothermic by 23 kJ/mol (5.5 kcal/mol). The conclusion that reaction 3 is unimportant is supported by the failure to detect absorption of CH_3 between 600 and 625 cm^{-1}.[13]

The presence of the absorptions of isolated HF and of rather prominent absorptions at 3422 and 3432 cm^{-1}, in the region appropriate for the stretching mode of HF perturbed by the formation of a relatively strong hydrogen bond, indicate that H-atom abstraction also occurs. The frequency ratio of the 2532-cm^{-1} peak of the F + CD_3ONO experiments to this pair of peaks equals 0.74, appropriate for the assignment of the 2532-cm^{-1} peak to the corresponding DF-stretching absorption. However, although the 3422–3432-cm^{-1} absorptions were prominent in the initial deposit and grew somewhat on photolysis, the 2532-cm^{-1} peak appeared only after the sample had been photolyzed. The 695-cm^{-1} peak is in the spectral region appropriate for assignment to one of the HF-deformation modes of a hydrogen-bonded complex. The 515-cm^{-1} peak which appeared on photolysis of deuterium-substituted

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(29) G. Inoue, H. Akimoto, and M. Okuda, *J. Chem. Phys.*, **72**, 1769 (1980).

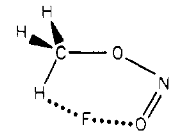
samples also has a frequency ratio of 0.74 with respect to the 695-cm^{-1} peak, suggesting that these two peaks may be contributed by DF- and HF-deformation vibrations of the complex. The differing photolytic behavior of the absorptions here attributed to the HF and DF complexes with species A will be considered in the following discussion.

Peaks were also present at 1500, 1722, and 1741 cm^{-1} in the spectra of unphotolyzed Ar:CH_3ONO + F deposits. The 1500- and 1741-cm^{-1} peaks lie at the positions of the most prominent absorptions of H_2CO isolated in solid argon, suggesting that reactions 1a and 1b may occur to a significant extent during the approximately 10^{-4} s[14] during which F atoms can react with CH_3ONO before the sample is frozen onto the cryogenic surface. The weak to moderately intense 1699-cm^{-1} absorption in the F + CD_3ONO experiments can also be assigned to isolated D_2CO. The 1722-cm^{-1} peak of the CH_3ONO studies lies 19 cm^{-1} below the peak of isolated H_2CO and the 1678-cm^{-1} peak of the CD_3ONO studies 21 cm^{-1} below the isolated D_2CO absorption. Since, within the combined experimental error, the two frequency shifts are similar, it is suggested that the 1722- and 1678-cm^{-1} peaks are contributed by perturbed H_2CO and D_2CO, respectively. The observation that the 1500-cm^{-1} peak is more intense than the 1741-cm^{-1} peak, whereas for isolated H_2CO the reverse is true, is also consistent with the assignment of the 1722-cm^{-1} peak to perturbed H_2CO, since the 1500-cm^{-1} H_2CO peak has generally shifted very little in experiments in which hydrogen-bonded H_2CO is formed. Among these systems are the $H_2CO\cdots HF$ complex, with absorptions at 1733 and 3570 cm^{-1},[15a] and the $H_2CO\cdots HNO$ complex, with its most prominent H_2CO absorption at 1736 cm^{-1}.[24,25] On photolysis of the products of the reaction of F atoms with CH_3NO_2 isolated in an argon matrix, an absorption appeared at 1731 cm^{-1} which was attributed to H_2CO perturbed by both NO and HF trapped in nearby sites.[5] No HF-stretching absorption was observed for this ternary interaction system, but it was suggested that such an absorption might have been obscured by the extremely strong absorption of $CH_2NO_2\cdots HF$ near 3520 cm^{-1}.

While the assignment of the 1722- and 1678-cm^{-1} peaks to perturbed H_2CO and D_2CO, respectively, seems straightforward, the nature of the perturbation remains somewhat obscure. The expected products of reactions 1a and 1b occurring in the solid are H_2CO + NO + HF, the same products as were reported to have been formed by the photodecomposition of $CH_2NO_2\cdots HF$. A precedent for the occurrence of two distinct types of site in which the hydrogen-bonding interactions differ significantly has been provided by studies of the $H_2CO\cdots HNO$ interaction.[24] The substantial exothermicity of reactions 1a and 1b may result in the occurrence of local annealing. Such a process would be less likely in the F + CH_3NO_2 experiments, in which H_2CO is formed by the photodecomposition of the relatively stable CH_2NO_2 free radical.[5] Another explanation is based on the observation that the 1722- and 1678-cm^{-1} peaks grow under photolysis conditions which also result in the decomposition of CH_3ONO and in the stabilization of $H_2CO\cdots HNO$ in the solid. Conceivably F atoms preferentially attack the relatively weakly bonded H atom of HNO, leading to a unique orientation of the resulting HF and NO molecules with respect to H_2CO.

The changes in intensity of the peaks attributed to the A$\cdots$HF complex when the sample is photolyzed parallel those of the 1722-cm^{-1} perturbed H_2CO absorption, consistent with the assignment of the A$\cdots$HF absorptions to the ternary $H_2CO\cdots NO\cdots HF$ complex. However, the 1678-cm^{-1} perturbed D_2CO absorption grew more slowly than did the A$\cdots$DF absorptions, casting doubt on such an assignment. Alternatively, species A may be CH_2ONO, with infrared absorptions which are weak relative to those of the HF or DF in its hydrogen-bonded complex.

The detection of prominent A$\cdots$HF absorptions in the initial deposit but the requirement of photolysis for the development of the corresponding absorptions of A$\cdots$DF parallels the isotopic behavior of the F + CH_3NO_2 reaction system.[5] While very prominent $CH_2NO_2\cdots HF$ absorptions were present in the initial F + CH_3NO_2 deposit, photolysis was required to decompose the weakly bound $CD_3NO_2\cdots F$ complex which was intermediate in the formation of $CD_2NO_2\cdots HF$. This difference was attributed to the decomposition of the initially formed $CH_3NO_2\cdots F$ complex by a tunneling mechanism. In the present experiments, a six-center complex of the form



might be envisioned. Tunneling decomposition would be much less probable for the deuterium-substituted complex, which may require photoexcitation to facilitate its decomposition into either $CD_2ONO\cdots DF$ or $D_2CO\cdots NO\cdots DF$. However, it should be noted that the chain structure of *trans*-CH_3ONO would not favor the formation of such a cyclic addition complex. The slightly more stable cis rotamer would, of course, be more likely to form a structure such as that above. The "eclipsed" form of *cis*-CH_3ONO present in the proposed cyclic complex was found in the microwave studies of Turner and co-workers[30] to be less stable than the "staggered" form, in which the H atom in the plane of symmetry of the molecule is on the opposite side of the C-O bond from the nitrosyl oxygen. The barrier to the rotation of the methyl group, found in the microwave studies to be exceptionally low for the trans rotamer, is exceptionally high (8.7 kJ/mol, or 2.1 kcal/mol) for the cis species.[30,31]

The existence of such a barrier to the formation of a cyclic complex, intermediate in reaction 1a, may help to explain the important role found for the reaction channel in which FON is formed, which would be substantially less exothermic than either reaction 1a or reaction 2.

The tunneling mechanism for the decomposition of the complex would also help to explain the deuterium-isotopic dependence of the FON:FNO ratio. In the F + CD_3ONO experiments, the FON absorptions were somewhat stronger than the nearby FNO absorptions, whereas in the F + CH_3ONO experiments the reverse was true. The elimination of HF from the cyclic intermediate in the gas phase followed by reaction 1b would provide a source of NO, which could then react with F atoms to form either FNO or FON. Such a source of NO would play a much less important role in the deuterium-substituted system.

Conclusions

Two reaction channels are important in the reaction of F atoms with CH_3ONO. The more exothermic of these is H-atom abstraction. There is some evidence for the formation of a cyclic complex which eliminates HF by a tunneling mechanism. Even when trapped at 14 K, the CH_2ONO is marginally stable against decomposition into

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$H_2CO + NO$. The less exothermic initial reaction channel, involving NO abstraction, leads to the selective appearance of two infrared absorptions previously assigned by Smardzewski and Fox[20-22] to FON, supporting the identification of this species. However, the previous assignment of the NO-stretching fundamental of FON is not confirmed.

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Registry No. Ar, 7440-37-1; F, 14762-94-8; CH_3ONO, 624-91-9; FON, 87261-91-4; FNO, 7789-25-5; HF, 7664-39-3; H_2CO, 50-00-0; HNO, 14332-28-6; NO, 10102-43-9; FNO_2, 10022-50-1; CD_3ONO, 63562-23-2; DF, 14333-26-7; D_2CO, 1664-98-8; DNO, 16355-69-4; NF_3, 7783-54-2; NF, 13967-06-1; NF_2, 3744-07-8; CH_2ONO, 87261-92-5.

Rate Constants for the Addition of OH to Aromatics (Benzene, *p*-Chloroaniline, and *o*-, *m*-, and *p*-Dichlorobenzene) and the Unimolecular Decay of the Adduct. Kinetics into a Quasi-Equilibrium. 1

A. Wahner and C. Zetzsch*

Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, Postfach 102148, D-4630 Bochum 1, West Germany

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Using pulsed vacuum-UV photolysis of H_2O at $\lambda > 125$ nm for the production of, and time-resolved resonance fluorescence for the detection of, OH, we determined rate constants for the reactions of benzene, *p*-chloroaniline, and *o*-, *m*-, and *p*-dichlorobenzene with OH at room temperature, yielding the following values ($k \pm 3\sigma$, in units of 10^{-13} cm^3 s^{-1}): 8.8 ± 0.4, 830 ± 42, 4.2 ± 0.2, 7.2 ± 0.2, and 3.2 ± 0.2 in Ar at 133 mbar. The decays of OH in the presence of the aromatics are observed to be biexponential. The system of differential equations related to the reaction mechanism is solved. The rate constant of the unimolecular decay of the OH–benzene adduct is determined to be strongly temperature dependent, yielding values of 1.95 ± 0.2 and 11.5 ± 1 s^{-1} at 295 and 312 K.

Introduction

Reactions of OH with aromatics[1] and chlorinated benzenes[2] are important for chemical models of tropospheric air pollution. At room temperature and below these reactions mainly proceed through addition. They may be taken as fundamental examples for reactions leading to a steady state not far from equilibrium.

Absolute and relative rate constants for the reaction of OH with benzene (including its dependence on temperature and pressure) have been determined previously by several groups.[3-12] Models considering the competing channels (abstraction of H, addition of OH, and subsequent decay of the adduct) have resulted from the observation of a complicated temperature dependence of the overall rate constant and of nonexponential decays of OH.[7,8]

The present study will report on measurements of rate constants for the reactions of OH with benzene, with the three isomeric dichlorinated benzenes, and with *p*-chloroaniline.[10] An improved detection limit for OH in our apparatus[10] allows us to observe OH at long reaction times up to 3 s. A quantitative method of evaluating the unimolecular decay of the aromatic–OH adduct by solving the differential equations for the competing processes—abstraction, addition, unimolecular decay of the adduct, and diffusional loss (of OH and the adduct)—will be presented.[12] Experimental findings with benzene and the model agree in that the nonexponential decays of OH observed previously[7,8] are biexponential decays to a very good approximation.

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