715 cm⁻¹ shoulder as B_2 or B_3 . It may also be possible that the shoulder at 690 cm^{-1} is better assigned as B_1 and belonging to BrF_2^+ . Finally some of the *B* modes originating in v_3 and v_1 are found at 673, 663, and 638 cm⁻¹ and again coupling and superposition may occur.

A similar approach cannot be used for the two remaining compounds ClO₂SbF₆ and ClF₂SbF₆ where the crystal structures are unknown.

The previous interpretation of the ClF_2SbF_6 spectrum (8) has invoked an identical molecular model as found for BrF_2SbF_6 (10). This is not confirmed by the vibrational spectra of bothcompounds. The apparent dissimilarity between the vibrational spectra for both compounds can have various reasons such as different crystal structures, a weaker ClF₂⁺ linkage so that not coupling of vibrations can occur, or an entirely different molecular structure. The splittings found for v_3 and v_2 and the relaxation of the mutual exclusion rule for the 647 cm^{-1} band are in our opinion sufficient evidence for anioncation interaction.

No certain assignment is possible for SbF_6^- in ClO₂SbF₆. Strong Raman active bands are found at 706, 680, and 649 cm⁻¹ in the region of v_1 . Here, v_2 appears not to be widely split; the small splitting of 4 cm^{-1} may possibly be caused by the crystalline field. These features are difficult to reconcile but again departure from an ionic model is apparent. Similar features as the shift of the anion frequencies to higher wavelengths are also

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found for $(ClO_2)_2SnF_6$ and are discussed there more fully (16).

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The reaction of acetic acid and nitrogen dioxide

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Nitric oxide was found to be an autocatalyst in the reaction of acetic acid and nitrogen dioxide at 470 and 527 °K in the vapor phase. The observed products, in addition to NO, were \overline{CO} , CO_2 , and CH₃NO₂.

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Autocatalysis by NO was observed in the reaction of NO_2 with formic acid (1) but not in the reactions of NO₂ with formaldehyde (2), acetaldehyde (3), glyoxal (4), and some other organic molecules. The peculiar hydrogen kinetic isotope effects which were found in the reaction of NO₂ with formaldehyde were interpreted in terms of a chain mechanism (5). However, the origin of the hydrogen isotope effects in the reaction of NO_2 with formic acid is still obscure (6) and the

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Exp. No.	CH3COOH		NO_2			Product, moles $\times 10^6$				
	P_0	No	P_0	No	$\Delta P_{\rm f}$	co	CO2	CH ₃ NO ₂	NO	$\Delta P_{\rm o}/\Delta t$
1†	19.3	119	16.2	100	13.5	12	54	8	88	3.5
2†	19.6	121	27.9	173	23.0	24	85	13	164	5.3
3‡	19.6 ± 0.1	121 ± 1	60.7 ± 0.5	376 ± 5	46.8 ± 0.6	62 ± 1	152 ± 1	30 ± 1	§	10.7 ± 1.2
4	19.6	121	86.9	537	47.7	61	159	§ _	§	20.0
5	10.2	63	59.8	369	24.3	29	82	22	§	7.0
6	10.8	67	59.9	372	§	Ş	ş	§	Š	6.2
7†	45.4	281	60.8	376	45.1	50	172	53	312	15.0
8†	45.5	281	60.0	371	45.4	58	168	ş	307	12.0
9†	95.7	592	60.7	375	39.5	ş	Ş	Š	ş	29.0
10†	95.7	592	60.4	374	35.5	ā	Š	Š	Š	23.5

				INDLE I				
Summary	of th	e results	of	complete	reactions	at	526.5	°K*

* P_{0} , initial pressure in mm Hg; N_0 initial concentration in moles $\times 10^6$; ΔP_f , final pressure change in mm Hg; $\Delta P_0/\Delta t$, initial rate of pressure rise in mm Hg s⁻¹. †Excess acetic acid. ‡Results in this row are average of 5 to 8 runs. \$No analysis.

mechanism of the autocatalysis is unknown. The possibility was considered that autocatalysis is specifically related to the carboxyl group. In order to test this hypothesis information on the reactions of NO_2 with other carboxylic acids is required. In this note some results of an exploratory study of the reaction of NO₂ with acetic acid are reported. Further details may be found in ref. 7.

40 30 P (mm) ٩ 20 +O ю 20 30 TIME (IOO s)

Experimental

The apparatus and procedure were similar to those previously described (6). Glacial acetic acid and acetic acid prepared from acetic anhydride were used. Acetic acid-d (CH₃COOD) was prepared from acetic anhydride and D₂O (7).

The products were divided into three fractions, the first collectable by toepler pump at -220 °C, the second at -120 °C, and finally the residue. The first fraction, mainly CO, was oxidized over hot CuO. The second fraction, mainly CO2 and NO, was analyzed using a trap at -160 °C. The residue was analyzed for CH₃NO₂ in a gas infrared cell with CaF2 windows. Attempts were made to detect N2O in the CO2 by means of gas chromatography using a silica gel column, and by using caroxite.

Results

Examples of pressure-time curves at 526.5 °K are illustrated in Fig. 1. Product yields, pressure changes, and initial rates of pressure change are listed in Table 1. Mole fractions of products assumed to arise from the methyl group are listed in Table 2. The cumulative analytical errors are such that about 5% of the nitrogen or of the carbon could be present as products other than CO, CO₂, CH₃NO₂, or NO. Small amounts of N₂ or of N_2O were suspected in the CO and CO_2



fractions, respectively, but were not identified and if present do not exceed 1% of the total nitrogen.

The rates of pressure rise are not particularly useful because of the complicated stoichiometry

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	TA	BLE 2					
	Fate of the	methyl gro	up*				
D	D	Mole fraction of methyl group products					
СН₃СООН	NO ₂	CO	CH ₃ NO ₂	CO			
19.6 19.6	16.2 27.9	0.32 0.39	0.22 0.21	0.46			
19.6 19.6 10.2	60.7 86.9 59.8	0.50 0.50 0.39	0.24 0.18 0.36	0.25 0.31 0.26			
45.4	60.8	0.36	0.38	0.25			

60.8 *Po, initial reactant pressures in mm Hg.

and also because of the concurrent decomposition of NO₂. In any further study of the reaction the technique of Gagarina and Emanuel might be used, in which NO_2 is added first and the NO_2 , O₂, and NO are allowed to approach equilibrium before the organic compound is added (8).

Experiments carried out at 470 °K, not reported here, gave results which were essentially the same as those at 527 °K.

Discussion

The shapes of the pressure-time curves are characteristic of autocatalytic reactions in which the rate expression contains a non-autocatalytic term, since the rate does not approach zero at zero time. In fact the curves resemble those observed for the reaction of NO₂ and formic acid (1, 6). The pressure-time curve of experiment 27, Fig. 1, with NO added initially, shows that NO is a catalyst. The results are consistent with the suggestion that the carboxyl group is related to catalysis by NO and indicate that further work should be profitable. However, since the oxidation of CH_4 by NO₂ is catalyzed by NO (at much higher temperatures) (8) the autocatalysis cannot be viewed as being due to some unique property of the carboxyl group.

The observation of a hydrogen isotope effect, as in experiment 28B, indicates the importance of carboxyl hydrogen abstraction.

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Since the quantity of CO₂ which is produced in experiments with excess NO₂ (Table 1) exceeds that available from the carboxyl group, the methyl group is partially oxidized to CO_2 . By assuming that the carboxyl group appears entirely as CO₂, the proportions of CO, CO₂, and CH₃NO₂ which are formed from the methyl group have been calculated and are listed in Table 2. Although reactions are known which are consistent in a qualitative way with the fate of the methyl group, the observed variation in the ratio $[CO_2]/$ [CO] as a function of pressure of NO_2 could not be accounted for. In columns 7-10 of Table 1 it can be seen that the final pressure change is smaller at a high pressure than at a low pressure of acetic acid, indicating that a high pressure of acetic acid favors formation of CH₃NO₂. This observation also could not be explained.

The results of this exploratory study indicate that a more detailed investigation should prove interesting in connection with reactions involving the methyl group as well as with the mechanism of autocatalysis.

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