50. Linear-Reactor-IR.-Matrix and Microwave Spectroscopy of the System $O_3/NO_2/(Z)$-2-Butene

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Summary

Investigation of the formation of complex reaction products in the gas-phase system $O_3/NO_2/(Z)$-2-butene by combination of linear reactors with IR. matrix and microwave *Stark* spectroscopy is reported. Besides the polyatomic products observed earlier in the gas-phase ozonolysis of (*Z*)-2-butene, the following products were identified: N_2O_5, HNO_3, HNO_4, CH_3NO_2, CH_3ONO, CH_3COONO_2 and $CH_3COO_2NO_2$ (peroxyacetyl nitrate, PAN). Matrix IR. spectra of N_2O_5, HNO_3, CH_3COONO, CH_3COONO_2 required for reference purposes are presented. It is shown that PAN-formation occurs already in the absence of light. A reaction scheme is proposed for explanation of the observed complex NO_x-containing products, which assumes methyldioxirane as a central intermediate. Particular reaction steps of the scheme will be discussed, including thermochemical estimates of reaction enthalpies.

1. Introduction. - The complex reactions induced by light in olefin/NO_x/air mixtures are considered to be the main body of the photochemical smog-formation process [1] [2]. Subsequently they have been the subject of intense kinetic investigations and kinetic modelling. Recent work and review on this aspect of the photosmog mechanism have been published by *Falls & Seinfeld* [2], *Akimoto et al.* [3], *Adashi et al.* [4], *Pitts & Finlayson-Pitts* [5] and others. Mechanism and kinetics of complex reaction product formation appear nevertheless comparatively little investigated in spite of the fact that they involve some of the most effective irritants like peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBN). These mixed carboxylic nitric anhydrides are assumed to usually emerge from reactions of peracyloxy radicals and NO_x (*cf.* [2]).

In the course of the study of complex reaction products of the gas-phase ozonolysis of ethylene and (*Z*)-2-butene a surprisingly wide variety of polyatomic products has been found [6] [7]. This finding raised the question whether the more complex systems involving NO_x do not produce a similar variety of reaction products related to nitrous, nitric and pernitric acid.

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In this work we wish to report experiments devoted to the detection of complex reaction products in the system O_3/NO_2/(Z)-2-butene in the absence of light. Applying the same techniques as in the earlier work, linear reactor - infrared matrix (LR.-IR.) and linear reactor-microwave (LR.-MW.), this system has been investigated under widely varying reaction conditions. Both (LR.-IR.)- and (LR.-MW.)-experiments were carried out with different reactors including a precision - all-quartz microreactor. Besides products already known from the O_3/(*Z*)-2-butene system unequivocal identification of the following complex products was proven by comparison with IR. matrix spectra of the pure compounds for N_2O_5, HNO_3, CH_3NO_2, CH_3ONO, CH_3ONO_2, CH_3COONO_2, PAN, HNO_4.

2. Experimental. - 2.1. *Chemicals.* (LR.-IR.)-experiments were carried out with Ar (*Linde*, purity 4.8, impurities: <3 vppm O_2, <5 vppm H_2O, <5 vppm N_2), O_2 (*Messer Griesheim*, purity 4.8), (*Z*)-2-butene (*Messer Griesheim*, purity 2.0; *Fluka*, purity 2.8) without further purification. NO_2 (*Messer-Griesheim*, purity 1.8) was purified by 3-5 trap to trap destillations over granulated P_2O_5 until the blue color characteristic for traces of water in NO_2 disappeared. The ozone was prepared with the aid of a *Fischer* ozonizer, adsorbed on silicagel at $-120°$ to $-115°$, separated from excess O_2 by pumping to a few mTorr and desorbed by flushing with Ar.

Diluted mixtures (600 Torr total pressure) of O_3 in Ar (partial pressure 0.1-30 Torr) were made by flushing the loaded silicagel with an Ar flow-up to 50 cm^3/min at an appropriately chosen desorption temperature. Similarly Ar/NO_2 mixtures were prepared either by static mixing of the component gases or by sorption ($\approx 20°$) and desorption of NO_2 on silicagel ($-15 \pm 5°$). (*Z*)-2-Butene/Ar mixtures were prepared by static mixing of the two components.

Acetyl nitrite (CH_3COONO) was prepared according to a method used by *Francesconi et al.* [8] based on the following reaction:

$$CH_3COOAg + NOCl \rightarrow CH_3COONO + AgCl.$$

Purification of this compound proved rather difficult owing to extremely fast hydrolysis by traces of H_2O. Characterization has been made by IR.-gas and -matrix spectra and by UV., NMR. and MS. routine spectroscopy. A typical UV.-absorption band near 385 nm ($\varepsilon_{max} = 4.0(5) \cdot 10^{-3}$ $Torr^{-1}$ cm^{-1}) should be noted, which might be considered as an analogue of the alkyl nitrite bands near 320-400 nm ($\varepsilon_{max} = 4 \cdot 10^{-3}$ $Torr^{-1}$ cm^{-1}). To our knowledge no UV./VIS. spectra of CH_3COONO are available in the literature.

Acetyl nitrate was obtained by following a preparation reported by *Pictet et al.* [9], using the following gas-phase reaction [10]:

$$(CH_3CO)_2O + N_2O_5 \rightarrow 2\ CH_3COONO_2$$

2.2. *Linear reactor-IR.-matrix experiments (LR.-IR.).* LR.-IR. spectra were produced along the lines reported in the earlier work [6] [7] or by means of the gas manifold shown in *Figure 1*, which served to produce the 3 Ar/reactant mixtures of appropriate pressure, composition and equal flow. As reactors the system described earlier was used, equipped with either a big cylindrical reactor (BR.) of 10 cm length and 1 cm diameter [7] or with the small reactor (SR.) shown schematically in *Figure 2.* The reactor chamber of the latter consists of exchangeable suprasil tubes (10 mm outer diameter) with various inner bore (0.75-3 mm diameter) and variable lengths (7.5-30 mm) yielding reactor volumina between 3.5-210 mm^3. The inlet of the gas streams is made through three capillary tubes of ≈ 0.1 mm laser bore; discharge is made either by a laser-drilled hole in a 0.2 mm quartz plate or through a metallic electron microscope nozzle (*Siemens*, single hole nozzles of 50 µm diameter) of appropriate bore.

In *Table 1* information on the reactor operation parameters of the LR.-IR. experiments is given including total pressure in the reactor, partial pressure of reactants and typical residence time. All experiments were carried out with the reactor kept at ambient temperature.

2.3. *Linear reactor-microwave spectroscopy (LR.-MW.).* All experiments were carried out in the setup reported earlier [6] [7], applying operation conditions as listed in *Table 1. Stark* spectroscopy was

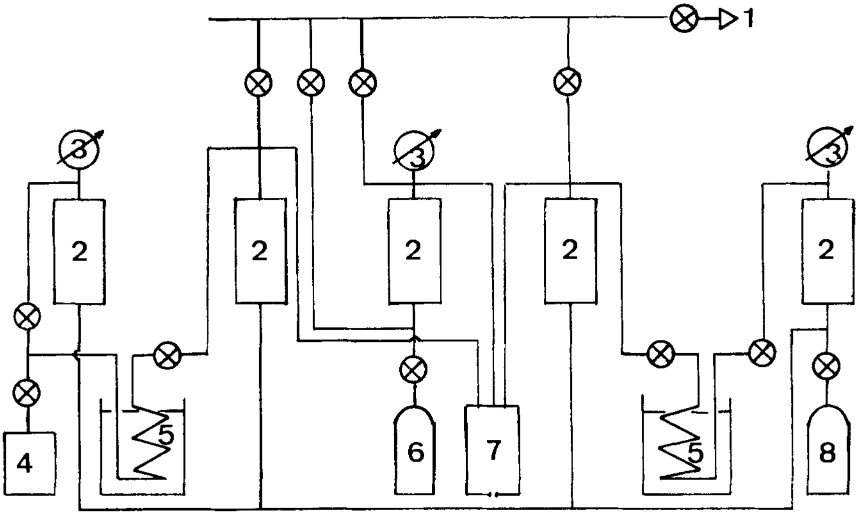

Fig. 1. *Vacuum-manifold for supply of reactant-Ar-mixtures* (1: to vacuum pump, 2: flow meters, 3: manometers, 4: Fischer ozonizer, 5: pyrex helix filled with silicagel for adsorption of O_3 and NO_2, 6: (*Z*)-2-butene/Ar mixture, 7: large and small reactor, 8: Ar-supply)

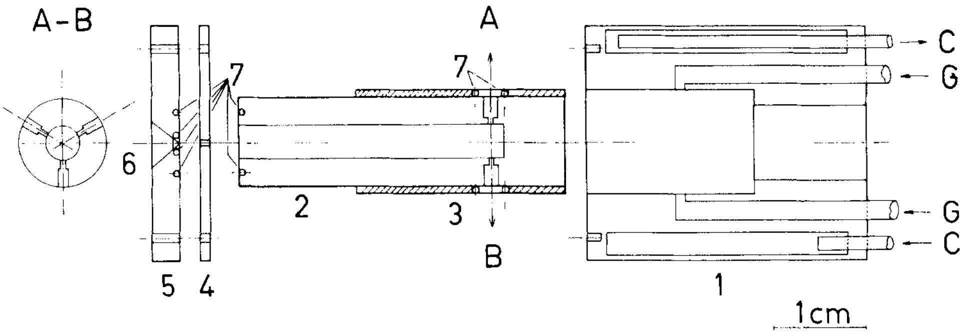

Fig. 2. *Small reactor - exploded view*
(G: gas inlet tubes, C: coolant inlet and outlet tubes, 1: stainless steel body serving as heat exchanger and holder, 2: quartz microreactor, 3: copper cylinder serving as heat conductor and light reflector, 4: Teflon plate, 5: stainless steelplate serving as holder for nozzle, 6: metallic electron microscope nozzle, 7: O-ring (VITON))

made with 60-80 mTorr total pressure in the waveguide (kept at ambient temperature). The spectra were recorded digitally, scanning each line 20-30 times and subjecting the data to signal-averaging and smoothing.

3. Results. - In *Table 2* a list of complex reaction products is presented, listing products as observed by particular experiments (LR.-IR. or LR.-MW.). The spectral features according to which each detected species was identified are collected in *Table 3*. *Figures 3* and *4* give reference IR. spectra of those compounds for which no matrix spectra are available from literature, and *Figure 5* shows LR.-IR. spectra

Table 1. *Typical experimental conditions of LR.-IR. and LR.-MW. experiments*

Type of experiment	Reactor type[a])	Operating conditions p_{tot} (Torr)	p_{O_3} (Torr)	p_{NO_2} (Torr)	p_{cB} (Torr)	V_R[b]) (cm^3)	τ_R[c]) (s)	ϕ_{tot}[d]) (cm^3 s^{-1})
LR.-IR.								
01/12 06/12[e]	BR.	600	8.6	3.5	7.5	8	140	0.056
08/07	SR.	640	1	1	1.1	0.21	1.9	0.11
09/07		660	2.1	1	1.1			
11/07		630	3	1.6	1.1			
LR.-MW.	WG.	4	2	1	1	31	30	1
		5	3	1	1			

[a]) BR.: big reactor, SR.: small reactor, WG: waveguide. [b]) Reactor volume. [c]) Residence time. [d]) Volume flow in reactor. [e]) Identical starting conditions as exper. 01/12, but reaction started 30 min after desorption of O_3, yielding an excess of (*Z*)-2-butene due to O_3-decay.

Table 2. *Dependence of production of complex species from $O_3/NO_2/(Z)$-2-butene system on initial composition*[a])

Exp. Nr.	Observed species
All LR.-IR.	O_3, NO_2, C_4H_8 H_2O, CO, CO_2 CH_4, CH_3OH, H_2CO, HCOOH, CH_3CHO, CH_3COOH, $(HCO)_2O$[b]) $CH_3COOCHO$[c]), SOZ[d]), CH_3COOOH N_2O_5, HNO_3, CH_3NO_2, *cis*- and *trans*-CH_3ONO, HNO_4, CH_3ONO_2, CH_3COONO_2, $CH_3COO_2NO_2$(PAN)
LR.-MW.	HNO_3, CH_3ONO_2, H_2O, H_2CO, CH_3OH, CH_3COOH, HCOOH, CH_3CHO
	Not observed species
LR.-IR. 01/12	N_2O_5, CH_3COONO_2
08/07	CH_3COOOH, HNO_3, HCOOH, CH_3COOH, $(HCO)_2O$, $CH_3COOCHO$
09/07	$(HCO)_2O$, $CH_3COOCHO$, CH_3ONO
11/07	$(HCO)_2O$, $CH_3COOCHO$, CH_3ONO

[a]) For initial partial pressures, see *Table 1*. [b]) Formic anhydride. [c]) Formic acetic anhydride. [d]) Secondary ozonide of (*Z*)-2-butene.

taken with the big reactor (BR.) and the small reactor (SR.) at approx. 600 Torr total pressure in the reactor (*cf. Table 1* for operating conditions).

In *Table 3* further information is given about the ratio of peak intensities of key bands relative to the following bands of CH_3CHO: 1748, 1349 and 506 cm^{-1}; only neighboring bands are compared. No quantitative information about ratios of product formation relative to CH_3CHO formation may be extracted from these peak ratios, owing to the lack of peak absorption coefficients of the products concerned. However, the ratios allow qualitative comparison of product concentrations observed in different SR. experiments.

In the LR.-MW. experiments only few of the complex reaction products observed in LR.-IR. experiments were identified. These are also listed in *Table 2*. For identification the same transitions as reported in the earlier (*Z*)-2-butene work were

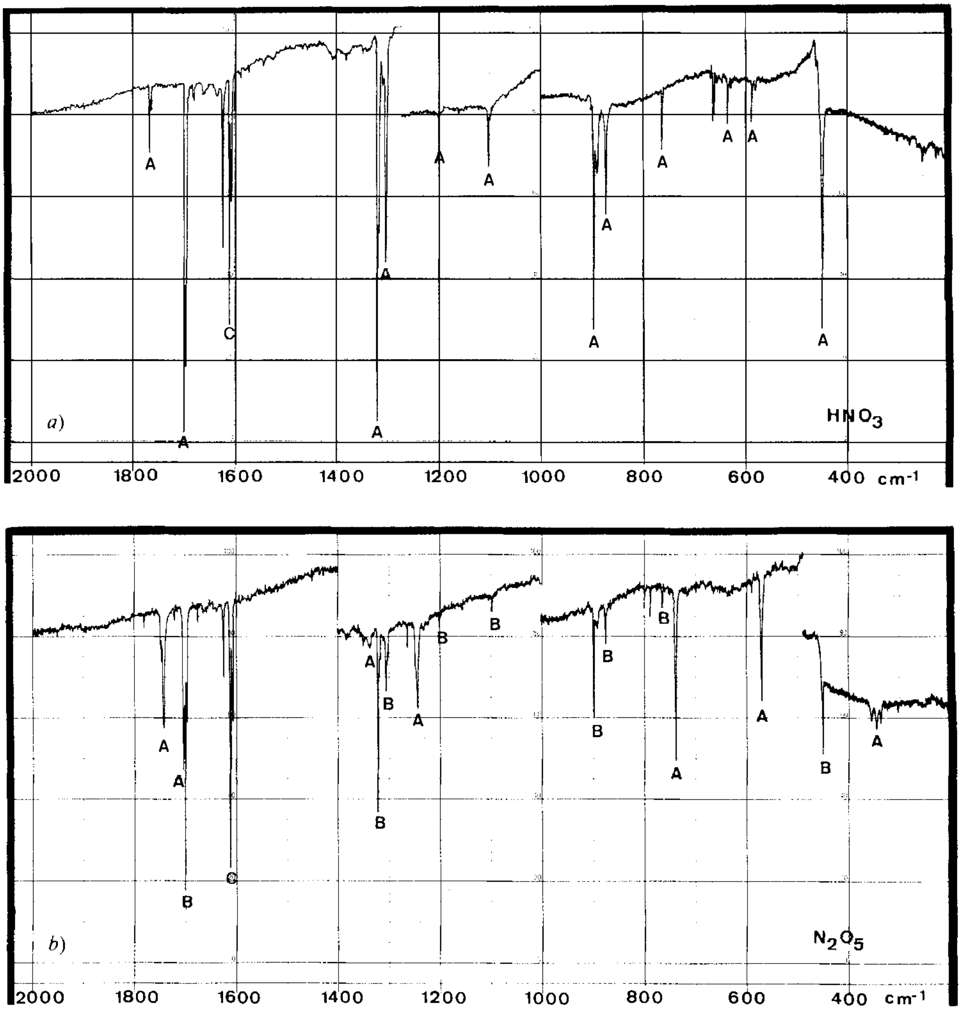

Fig. 3. *Reference IR. spectra of pure compounds in Ar-matrix at 4.2 K.*
a) HNO_3: M/A ratio 5000, A: HNO_3, C: NO_2; *b*) N_2O_5: M/A ratio 5000, A: N_2O_5, B: HNO_3, C: NO_2

used and therefore will not be reported here except for CH_3ONO_2 [7]. Methyl nitrate has been identified by the following transitions:

$3_{1,3}$-$4_{1,4}$	29766 MHz	$3_{1,2}$-$4_{1,3}$	34771 MHz
$3_{0,3}$-$4_{0,4}$	31149 MHz	$4_{1,4}$-$5_{1,5}$	36988 MHz
$3_{2,2}$-$4_{2,3}$	32461 MHz	$4_{0,4}$-$5_{0,5}$	38139 MHz
$3_{2,1}$-$4_{2,2}$	33894 MHz		

all lying in the R-band and determined by comparison with a reference spectrum[2]). It should be stated that intense search has been carried out for *cis*- and *trans*-HONO,

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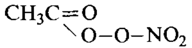
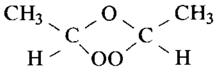
[2]) To our knowledge the R-band spectrum of CH_3ONO_2 has not yet been published.

Table 3. *Identification of complex reaction products by IR. bands in Ar matrices at 4.2 K*[a])

Chemical species	React. prod.		Rel.	Reference		Remarks
	$\tilde{\nu}$/cm^{-1}	intens.[b])	intens.[c])	$\tilde{\nu}$/cm^{-1}	intens.	
N_2O_5	1703	*vw*		1704	*s*	[10] [11]
	1244	*vw*		1244	*m*	
	738	*w*	0.2	737	*vs*	
	570	*w*	0.2	570	*s*	
HNO_3	1700	*vs*	2.1	1700	*vs*	[10] [12]
	1696	*s*		1696	*s*	
	1322	*s*	0.4	1322	*s*	
	898	*m*	0.5	897	*m*	
	450	*m*		451	*m*	
CH_3ONO *cis*	1613	*vw*		1613	*vs*	[13]
	838	*vw*		838	*vs*	
CH_3ONO *trans*	1665	*vw*		1665	*vs*	[13]
	1043	*vw*		1043	*s*	
	807	*vw*		807	*vs*	
CH_3NO_2	1574	*vw*		1574	*vs*	[14]
CH_3ONO_2	1656	*s*	1.4	1656	*s*	[15]
	1463	*w*		1465	*m*	
	1439	*w*		1440	*m*	
	1290	*s*	0.4	1290	*s*	
	1286	*m*		1286	*m*	
	1010	*m*	0.1	1011	*s*	
	856	*s*	0.9	854	*vs*	
CH_3COONO_2	1810	*m*	0.2	1810	*m*	[10]
	1719	*s*		1720	*vs*	
	1156	*m*	0.2	1156	*s*	
	799	*s*	0.9	799	*s*	
	722	*w*	0.2	722	*m*	
 $CH_3C{=}O\diagdown O{-}O{-}NO_2$ PAN[d])	1834	*m*	0.3	1833	*m*	[15]
	1731	*s*	1.7	1731	*s*	
	1722	*vw*		1723	*m*	
	1374	*w*	0.1	1374	*m*	
	791	*s*	1.3	790	*s*	
 SOZ[e])	1392	*m*	0.1	1393	*s*	[7]
	1147	*vw*		1147	*s*	
	1119	*w*		1119	*s*	
	522	*vw*		522	*m*	
HNO_4	1728	*vw*		1728	*vs*	[16]
	1396	*vw*		1397	*w*	
	1303	*w*		1304	*s*	
	804	*w*		803	*w*	
CH_3COONO	–	–		1788	*s*	[10]
	–	–		1749	*vs*	
	–	–		712	*s*	
	–	–		558	*m*	
	–	–		511	*s*	

[a]) Only those reaction products are listed which have not been observed in earlier work [6] [7].

[b]) Abbreviations: *vs:* very strong, *s:* strong, *m:* medium, *w:* weak, *vw:* very weak.

[c]) The relative intensity is the ratio of the peak absorbance of a certain compound to key bands of acetaldehyde. Three absorption bands of acetaldehyde in different frequency ranges have been chosen, namely from 2000-1500 cm^{-1} at 1748 cm^{-1}, from 1500-1000 cm^{-1} at 1349 cm^{-1}, from 1000-200 cm^{-1} at 506 cm^{-1}.

[d]) PAN = Peroxyacetyl nitrate.

[e]) SOZ = Secondary ozonide of (*Z*)-2-butene.

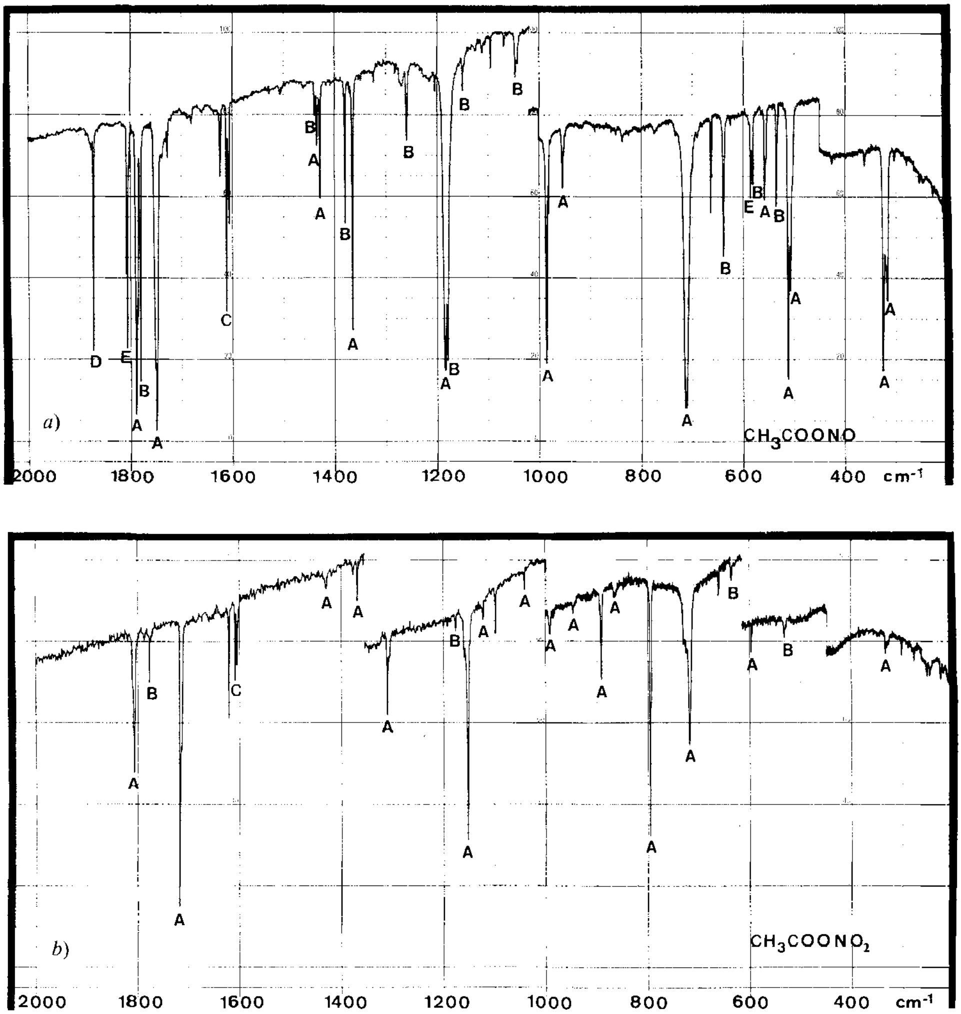


Fig. 4. *Reference spectra of pure compounds in Ar-matrix at 4.2 K.*
a) CH_3COONO(A): M/A ratio 3500;
b) CH_3COONO_2(A): M/A ratio 1500, B: CH_3COOH, C: NO_2, D: NO, E: NOCl

N_2O_5, CH_3NO_2, *cis*- and *trans*-CH_3ONO, C_2H_5ONO (several rotamers). None of these could be detected by microwave lines in the reaction spectra. For the other compounds containing nitrogen detected by LR.-IR. technique no reference spectra are known at the present time. Both CH_3COONO_2 and $CH_3COO_2NO_2$ and also N_2O_5 are expected to have low-lying vibrational states and probably will exhibit weak MW. spectra.

4. Discussion. – In our earlier work widely different conditions for LR.-IR. and LR.-MW. experiments were chosen, in particular with respect to the rate of de-

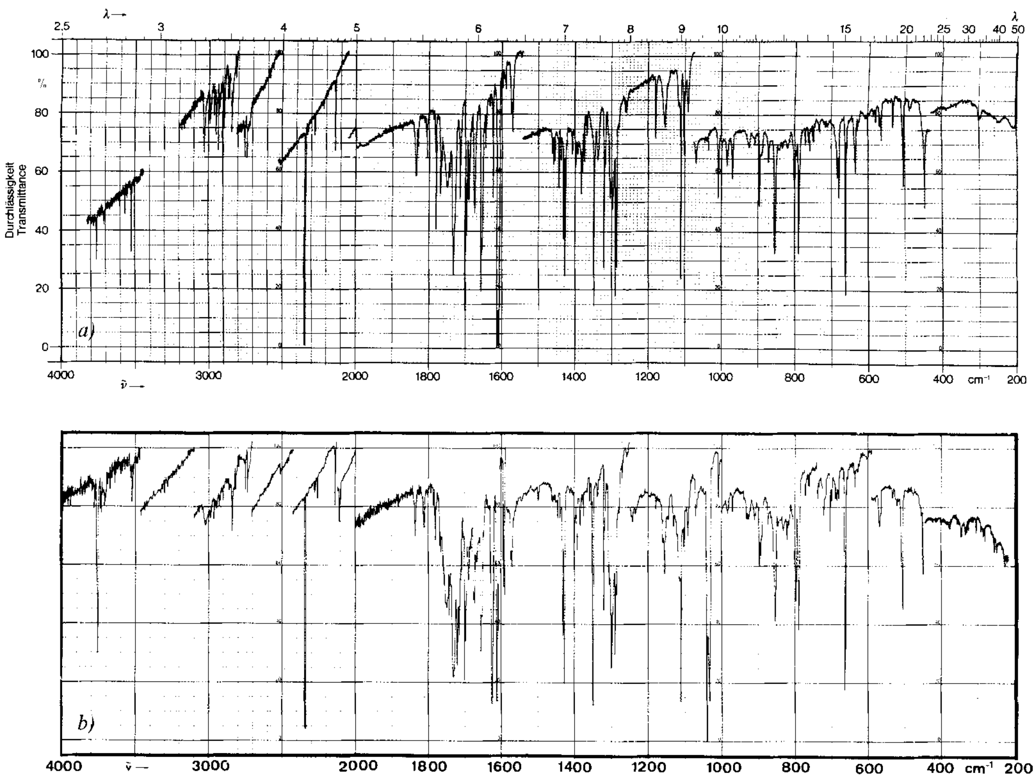


Fig. 5. *Linear reactor-IR.-matrix spectra of the system $O_3/NO_2/(Z)$-2-butene*
a) Big reactor, b) small reactor (*cf. Table 1* for operating conditions of reactors)

activation (pressure) and diffusion coefficients. In this way some judgment was obtained with respect to effects of radical reactions and wall effects [6] [7]. In the present work it has further been attempted to use reactors with widely differing operating characteristics within the IR. experiments.

4.1. *General features of LR.-IR. experiments.* As shown in *Table 1* the two reactor systems used for LR.-IR. experiments mainly differ with respect to the residence time (nearly two orders of magnitude) and partial pressure of reactants. Furthermore, the all-quartz construction of the small reactor should minimize the wall effects. Under the operating conditions of the two systems $t_{1/2}$- time and extent of reaction ξ of the ozone/(*Z*)-2-butene reaction ($k(298) \approx 1.6 \cdot 10^{-16}$ molecule^{-1} cm^3 s^{-1} [17], τ_R is residence time in reactor) amount to

$$\text{BR.: } t_{1/2} \approx 0.024 \text{ s}, \ \xi(\tau_R) \approx 1$$
$$\text{SR.: } t_{1/2} \approx 0.19 \text{ s}, \ \xi(\tau_R) \approx 0.9$$

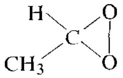
This difference may be responsible for discrepancies with respect to observed products. As typical examples the formic and formic acetic anhydrides should be mentioned which were not observable in the SR. experiments. In recent kinetic experiments with the $O_3 + C_2H_4$ reaction at high dilution by *Calvert et al.* [18], formic anhydride was formed at reaction time $t \approx t_{1/2} \gtrsim 30$ min. This should be contrasted with the experimental findings of this work with O_3/(*Z*)-2-butene, where anhydrides are observed at reaction times several orders of magnitude larger than $t_{1/2}$. The difference of anhydride production may originate from the widely different $\tau_R/t_{1/2}$ ratios for big and small reactor experiments (5000 and 10 respectively) in these two types of experiments.

Tables 1 and *2* further document that there are some marked differences between BR.- and SR. experiments, which will be discussed in relation to specific reaction products. Observation of CH_3OH is rendered difficult by coincidence with key bands (1443 and 1034 cm^{-1}) of (*Z*)-2-butene and O_3. Since the 1034 cm^{-1} band of CH_3OH/Ar appears to be accompanied reproducibly by a site-satellite at 1027.5 cm^{-1} [19], the latter band has been used for detection of CH_3OH.

4.2. *General features of LR.-MW. experiments.* For the system O_3/NO_2/(*Z*)-2-butene the LR.-MW. technique could not contribute independent information on NO_x compound-formation. Some reasons for this have been mentioned above. Nevertheless, some additional remarks should be made: *i*) in agreement with kinetic modelling, NO_2 nearly falls below the detection level under the conditions given in *Table 1; ii*) the measurement of the concentration of reaction products was hindered by strong fluctuation of signals, which so far could not be reduced; *iii*) in model experiments with the system O_3/NO_2 ($p_{O_3} \approx p_{NO_2} \approx 1$ Torr) essentially only HNO_3 was found ($p_{HNO_3} \approx 40$ mTorr at $p_{tot} \approx 60$ mTorr in the *Stark* cell). No microwave lines of N_2O_5 were detected, likewise no such lines could be identified even if N_2O_5 was introduced into the waveguide; *iv*) a number of lines have been found in LR.-MW. experiments, which so far have not been attributable to known species (MHz): 38962*s*, 38958*s*, 38322*w*, 38157*w*, 34100*s*, 28975*s*. Possible candidates responsible for these spectral features are HNO_4 and perhaps N_2O_5. Pernitric acid is assumed to play a possibly relevant role in tropospheric chemistry [20].

4.3. *Mechanisms of complex product formation.* - 4.3.1. *General considerations.* All compounds listed in *Table 2* which do not contain nitrogen have been observed in the O_3/(*Z*)-2-butene system. For these possible formation reactions have been suggested in our earlier work [6] [7]. The discussion of possible mechanisms of complex reaction products observed in this paper will therefore be restricted to N-containing species. A tentative reaction scheme will be presented which should explain the formation of the observed organic N-compounds without irradiation with light. It should first be mentioned that direct reaction of the olefin with NO_2 is too slow to be relevant in the experiments considered in this work. Such reactions have been studied earlier by *Michael et al.* [21] in gas- and liquid-phase and found to have typical $t_{1/2}$-times of the order of some hours at 40°. In this work the reaction NO_2 + (*Z*)-2-butene in the gas-phase has been found to possess $t_{1/2}$-times of ≈ 1 h. Since the residence time in our reactors amounts to maximally 140 and 1.9 s for BR. and SR., respectively, the direct reaction of olefin and NO_2 may be neglected.

In *Scheme 1* discussed below it will be assumed that the particle methyldioxirane



plays a central role in the formation of the various complex reaction species. This particle has not yet been observed directly in reactions of O_3 with (*Z*)-2-butene but the formation of its homologue $\overline{CH_2OO}$ has been proven in the (solid-state) reaction of O_3 and ethylene [22]. In earlier papers from this laboratory the oxirane species has been attributed a central role as an intermediate of the ozonolysis process, since uni- or bimolecular processes of the dioxirane leading to all observed reaction products may be formulated [6] [7]. Consideration of methyldioxirane as a central intermediate of the $O_3/NO_2/(Z)$-2-butene system with respect to formation of complex products therefore appears to be justified.

In the discussion only reactions are included which might be considered characteristic for the $O_3/NO_2/(Z)$-2-butene system, in particular those which lead to compounds derivable from NO_2 and other N-oxides. For the other observed polyatomic products reactions explaining their formation have been suggested in our earlier paper on the $O_3/(Z)$-2-butene system.

Before entering into the discussion of the formation reactions of nitro-, nitrate- and nitrite-compounds, the following reactions involving NO_2, O_3 and H_2O should be considered (*Scheme 1*).

Scheme 1

$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_2 + NO_3 \rightarrow N_2O_5$
$N_2O_5 \rightarrow NO_2 + NO_3$
$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$
$NO + NO_3 \rightarrow 2\ NO_2$
$NO + NO_2 \rightarrow N_2O_3$
$NO_3 + O_3 \rightarrow NO_4 + O_2$
$N_2O_5 + H_2O \rightarrow 2\ HNO_3$
$HNO_3 + NO_3 \rightarrow HNO_4 + NO_2$

The reactions comprised in *Scheme 1* constitute essentially the mechanism for N_2O_5-formation and decomposition. It appears plausible to assume that the dominant particles in this partial *Scheme* are O_3, NO_2, N_2O_5, which subsequently will be assumed to be the particles interacting with the dominant particles of the (*Z*)-2-butene ozonolysis reaction system.

Most of the complex reaction products of the $O_3/(Z)$-2-butene system are observed also in the $O_3/NO_2/(Z)$-2-butene system. It therefore may be assumed that the presence of NO_2 (besides competition for O_3) does not alter drastically the main characteristics of the first steps leading to the dioxirane. Model calculations for the system $O_3/NO_2/C_2H_4$ support this view [23]. However, the N-compounds of *Scheme 1* are expected to compete strongly by bimolecular reactions for the dioxirane and possible nonradicalic and radicalic products of it.

4.3.2. *Reaction scheme. Scheme 2* comprises a set of reactions which should explain the observed N-containing reaction products. For each of the latter a number of formation reactions may be considered which will be discussed in connection with particular compounds. For most of these estimates of ΔH°_{298} will be given [24]. Thermochemical estimates not available from literature will be briefly summarized in the *Appendix*.

1. *CH_3NO_2*. The reactions leading to CH_3NO_2 included in *Scheme 2*

$$CH_3\overline{CHOO} \rightarrow CH_3 + H + CO_2 \qquad (1)$$

$$CH_3 + NO_2 \rightarrow CH_3NO_2 \qquad (2)$$

and
$$CH_3\overline{CHOO} + N_2O_5 \rightarrow HCOO_2NO_2 + CH_3NO_2 \tag{3}$$

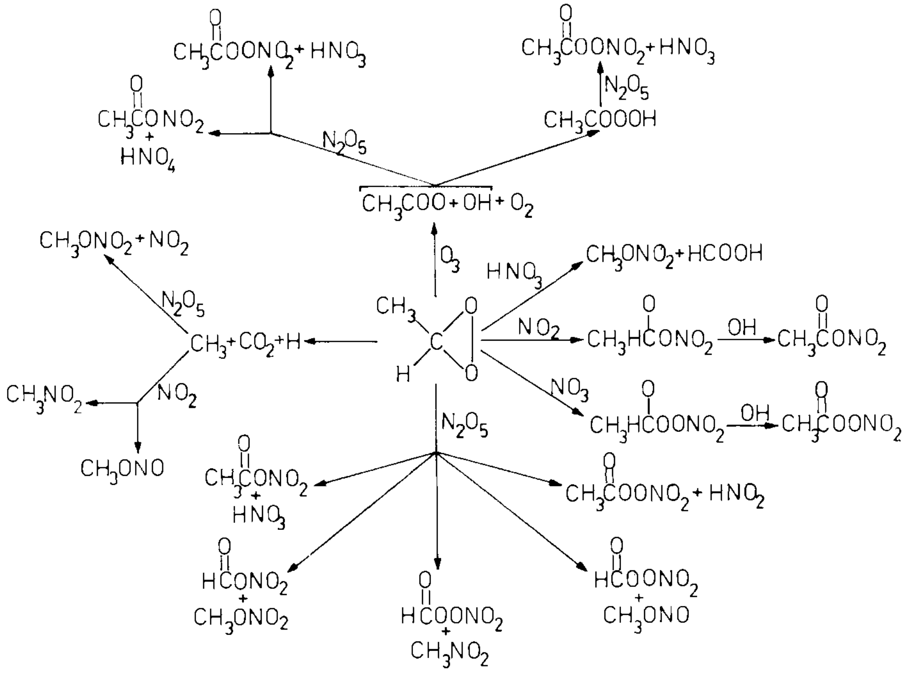
feature reaction enthalpies ΔH°_{298} of $+1$, -60 and -50 kcal, respectively. In the last value an estimate for ΔH°_{298} of $HCOO_2NO_2$ (peroxyformyl nitrate) has been applied. The first reaction competes the isomerization

$$CH_3\overline{CHOO} \rightarrow CH_3COOH \tag{4}$$

($\Delta H^\circ_{298} \approx -94$ kcal/mol). Though the latter is highly exothermic, there exists apparently no low-lying transition state for it in contrast to the first reaction. For this a nonadiabatic low-lying transition state has recently been found [25]. Furthermore the fact that only small amounts of CH_3COOH are found at reaction times of the order of seconds supports the relevance of the reaction (1). *Reaction 2* may be considered as a sink of methyl radicals in the photosmog process, since its rate constant is of the order of $3 \cdot 10^{-11}$ molecule^{-1}cm^3 s^{-1} [17]. Formation *via Reaction 3* would imply peroxyformyl nitrate, which has so far not been identified in this work and also has not yet been found in the photosmog process, probably owing to its expected high reactivity. Many more reactions might be possible producing CH_3NO_2, *e.g.*

$$CH_3\overline{CHOO} + N_2O_5 \rightarrow HCO + CH_3NO_2 + NO_4$$
$$CH_3\overline{CHOO} + NO_2 \rightarrow CO + CH_3NO_2 + OH$$
$$CH_3 + N_2O_5 \rightarrow CH_3NO_2 + NO_3,$$

or reactions involving N_2O_3, HNO_2 which, however, appear of less importance.


Scheme 2. *$O_3/NO_2/(Z)$-2-butene system: proposal for NO_x containing complex product formation reactions* (partial reaction scheme)

2. *CH_3ONO.* The formation of methyl nitrite according to

$$CH_3 + NO_2 \rightarrow CH_3ONO \tag{5}$$

or

$$CH_3\overline{CHOO} + N_2O_5 \rightarrow HCOO_2NO_2 + CH_3ONO, \tag{6}$$

will have reaction enthalpies of similar magnitudes as for CH_3NO_2-formation. No kinetic data for the radical combination reaction 5 seems to be available, but its rate constant may be expected similar to that of reaction 2. Again further reactions may be conceived leading to methyl nitrite, *e.g.* analogues to the reactions producing CH_3NO_2.

3. *CH_3ONO_2.* This molecule may be produced by *Reactions* like *7-11:*

$$CH_3\overline{CHOO} + N_2O_5 \rightarrow HCOONO_2 + CH_3ONO_2 \tag{7}$$

$$CH_3\overline{CHOO} + HNO_3 \rightarrow CH_3ONO_2 + HCOOH \tag{8}$$

$$CH_3 + N_2O_5 \rightarrow CH_3ONO_2 + NO_2 \tag{9}$$

$$CH_3 + O_3 \rightarrow CH_3O + O_2 \tag{10}$$

$$CH_3O + NO_2 \rightarrow CH_3ONO_2 \tag{11}$$

with the following reaction enthalpy values:

$\Delta H^\circ_{298}(7) = -74$ kcal, $\Delta H^\circ_{298}(8) = -77$ kcal,
$\Delta H^\circ_{298}(9) = -58$ kcal, $\Delta H^\circ_{298}(10) = -65$ kcal, and
$\Delta H^\circ_{298}(11) = -40$ kcal, all being highly exothermic.

The reaction product $HCOONO_2$ (formyl nitrate) has so far not been observed experimentally. From analogy with the high rate of hydrolysis of acetyl nitrate it appears however unlikely that this mixed anhydride could be detected in either LR.-IR. or LR.-MW. experiments. For the rate constant $k_{(10)}$ of *Reaction 10* an upper limit may be estimated from known data [17]: $1 \cdot 10^{-12} < k_{(10)} < 1 \cdot 10^{-11}$ molecule^{-1} cm^3 s^{-1}.

4. *CH_3COONO_2.* A large variety of mechanisms may be formulated for the production of acetyl nitrate like

$$CH_3\overline{CHOO} + N_2O_5 \rightarrow CH_3COONO_2 + HNO_3 \tag{12}$$

$$CH_3\overline{CHOO} + NO_2 \rightarrow CH_3COONO_2 + H \tag{13}$$

$$CH_3\overline{CHOO} + O_3 \rightarrow CH_3COO + O_2 + OH \tag{14}$$

$$CH_3COO + NO_2 \rightarrow CH_3COONO_2 \tag{15}$$

$$\mathrm{CH_3COO + N_2O_5 \rightarrow CH_3COONO_2 + NO_3} \tag{16}$$

$$\mathrm{(CH_3CO)_2O + N_2O_5 \rightarrow 2\ CH_3COONO_2} \tag{17}$$

$$\mathrm{CH_3COOH + N_2O_5 \rightarrow CH_3COONO_2 + HNO_3} \tag{18}$$

$$\mathrm{CH_3CHO + OH \rightarrow CH_3CO + H_2O} \tag{19}$$

$$\mathrm{CH_3CO + N_2O_5 \rightarrow CH_3COONO_2 + NO_2} \tag{20}$$

$$\mathrm{CH_3\overline{CHOO} + HNO_3 \rightarrow CH_3COONO_2 + H_2O} \tag{21}$$

The reaction enthalpies are as follows:

$\Delta H^\circ_{298}(12) = -97$ kcal, $\Delta H^\circ_{298}(13) = -19$ kcal
$\Delta H^\circ_{298}(14) = -65$ kcal, $\Delta H^\circ_{298}(15) = -30$ kcal
$\Delta H^\circ_{298}(16) = -9$ kcal, $\Delta H^\circ_{298}(17) = -9$ kcal
$\Delta H^\circ_{298}(18) = -3$ kcal, $\Delta H^\circ_{298}(19) = -33$ kcal
$\Delta H^\circ_{298}(20) = -61$ kcal, $\Delta H^\circ_{298}(21) = -88$ kcal

This is the first time that acetyl nitrate has been identified in a NO_2/O_3/olefin system. The IR. spectrum of the pure compound is shown in *Figure 4b*. Traces of acetic acid and NO_2 can be seen since the compound is very easily decomposed (hydrolyzed). However, no details on the decomposition mechanism can be given owing to the fact that no HNO_3 can be detected in reference spectra given in *Figure 4b*. Simple hydrolysis

$$\mathrm{CH_3COONO_2 + H_2O \rightarrow CH_3COOH + HNO_3} \tag{22}$$

$$\Delta H^\circ_{298}(22) \approx -6\ \mathrm{kcal}$$

should therefore be excluded. All of the above formulated reactions are exothermic. In experiments with BR. CH_3COONO_2 is not observed *(cf. Table 2)*, instead relatively large amounts of HCOOH, CH_3COOH and $HNO_3(NO_2)$ are found. This is probably due to the longer residence time, implying the more pronounced formation of H_2O and hydrolysis according to the foregoing equation.

5. *$CH_3COO_2NO_2$(PAN).* This molecule may be produced by *Reactions* like *23-31*

$$\mathrm{CH_3\overline{CHOO} + N_2O_5 \rightarrow CH_3COO_2NO_2 + HNO_2} \tag{23}$$

$$\mathrm{CH_3\overline{CHOO} + NO_3 \rightarrow CH_3COO_2NO_2 + H} \tag{24}$$

$$\mathrm{CH_3\overline{CHOO} + O_3 \rightarrow CH_3COO + O_2 + OH} \tag{14}$$

$$\mathrm{CH_3COO + N_2O_5 \rightarrow CH_3COO_2NO_2 + NO_2} \tag{25}$$

$$\mathrm{CH_3\overline{CHOO} + O_3 \rightarrow CH_3COOOH + O_2} \tag{26}$$

$$CH_3COOOH + N_2O_5 \rightarrow CH_3CO_2NO_2 + HNO_3 \tag{27}$$

$$CH_3COO + O_3 \rightarrow CH_3COO_2 + O_2 \tag{28}$$

$$CH_3COO_2 + NO_2 \rightarrow CH_3COO_2NO_2 \tag{29}$$

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \tag{19}$$

$$CH_3CO + O_2 \rightarrow CH_3COO_2 \tag{30}$$

$$CH_3\overline{CHOO} + HNO_3 \rightarrow CH_3COO_2NO_2 + H_2 \tag{31}$$

The enthalpy of each reaction is as follows

$\Delta H^\circ_{298}(23) = -71$ kcal, $\Delta H^\circ_{298}(24) = -13$ kcal
$\Delta H^\circ_{298}(25) = -4$ kcal, $\Delta H^\circ_{298}(26) = -104$ kcal
$\Delta H^\circ_{298}(27) = -15$ kcal, $\Delta H^\circ_{298}(28) = -25$ kcal
$\Delta H^\circ_{298}(29) = -26$ kcal, $\Delta H^\circ_{298}(30) = -36$ kcal
$\Delta H^\circ_{298}(31) = -18$ kcal.

The comparison of LR.-IR. experiments shows enhanced formation of PAN at longer residence times: taking CH_3CHO as a relative internal reference, approximately twice as much PAN is formed at 140 s residence time.

As a further point of interest it should be mentioned that PAN-formation exceeds apparently the formation of CH_3COONO_2. This possibly goes back to a faster reaction of the latter with H_2O. According to the findings of this work PAN is formed without photolytic steps, both in short and long residence-time experiments. This remarkable result might have some implications for PAN formation under the conditions of the photosmog process.

6. *N_2O_5*. Dinitrogen pentoxide is a characteristic transient particle of reaction *Scheme 1*. It is not observed at long residence times but is clearly identified at short reaction times. Again this may be explained by hydrolysis under the conditions of BR. experiments in which considerably stronger HNO_3 formation is noticed. Kinetic modelling calculation for *Scheme 1* predicts detectable concentrations of N_2O_5 at reaction times of the order of 10^2 s in the absence of H_2O. Furthermore, detectable concentrations of HNO_3 and N_2O_5 are predicted for this time range if $p_{H_2O}(0) \geq 0.1$ Torr, in qualitative agreement with BR. experiments.

4.4. *Unidentified spectral features.* In the LR.-IR. spectra a number of absorption bands were observed which, so far, could not be associated with known molecules. In *Table 4* a list of frequencies of unidentified bands is collected together with information on reactor conditions. There is little information available for assignment proposals. As an example the set of bands at 1786 (?), 1714, 1299 and 704 cm^{-1} (occurring at short residence times) can be mentioned which by analogy may be attributed to formyl nitrate. For this compound no reference spectrum is available for a definite identification. The proposal is in agreement with lack of $HCOONO_2$

Table 4. *Unidentified matrix-IR.-reaction bands of the O_3/NO_2/(Z)-2-butene system*

$\tilde{\nu}$/cm^{-1}	Intensity[a]		$\tilde{\nu}$/cm^{-1}	Intensity	
	SR.	BR.		SR.	BR.
1829	nd	*w*	1091	*m*	*m*
1806	nd	*m*	1070	*m*	*m*
1786	*w*	nd	931	*w*	*w*
1714	*vs*	nd	926	*w*	*w*
1690	*m*	*m*	913	*w*	*w*
1674	*s*	*s*	833	*w*	*w*
1367	nd	*m*	822	*w*	*w*
1359	*w*	nd	803	*m*	*m*
1340	*w*	*m*	704	*m*	nd
1298	*vs*	*m*	700	*w*	nd
1260	nd	*m*	681	*vs*	*m*
1154	nd	*m*	478	nd	*w*
1131	*w*	nd			

[a] Abbreviations: SR.: small reactor, BR.: big reactor, *w*: weak, *m*: medium, *s*: strong, *vs*: very strong bands, nd: not detected.

and abundant production of HCOOH at long residence times as a consequence of fast (homogeneous or wall-catalyzed) hydrolysis. *Table 4* might be useful in further experiments with O_3/NO_2/olefin systems.

4.5. *Role of radical reactions.* For both gas-phase ozonolysis and the photosmog process radical intermediates are generally considered to be important [26] [27]. Experimentally, however, only relatively little direct information on the existence of radicals has been given, *e.g.* for OH [28] [29], for HO_2 [30]. In a recent study by *Rakoczi et al.* [31] further radicals in the gas-phase ozonolysis of ethylene have been found by LR.-ESR. matrix spectroscopy, in particular H, CH_3, HO_2, NO_2, NO_3. Though these findings substantiate the kinetic importance of radicals, the possibility to detect radicals directly by LR.-IR. and LR.-MW. experiments seems to be small. Firstly, some of the radicals mentioned (OH, H, CH_3) are efficiently removed from the reaction space by wall reactions, and secondly, radical concentrations will, in general, remain below the limits of detection of both techniques [6]. Nevertheless reactions involving radicals (CH_3, OH, H, CH_3CO, CH_3COO) have been proposed in connection with *Scheme 2*. In the latter mostly non-radical processes have been suggested, but it should be clear that radical reactions could be formulated, leading to any of the observed complex NO_x-compounds. A more detailed consideration of radical mechanisms appears to be justified only if more definite information about the existence of further radical species is available.

Wall reactions might be relevant in the system O_3/NO_2/(Z)-2-butene with respect to (possibly catalyzed) hydrolysis of the mixed anhydrides of carboxylic acids and nitric acid, besides radical reactions. As has been discussed above, pertinent differences in product spectra of LR.-IR. and LR.-MW. experiments probably originate from such processes.

Appendix. - For the evaluation of thermochemical estimates of the mixed anhydrides of carboxylic and nitric acid (*e.g.* acetyl nitrate) and of the radicals CH_3COO, CH_3COO_2, no group contributions seem to be available in the literature. A derivation of such increments from existing estimates is shown below. The values should be considered as preliminary predictions.

Acetoxy radical (CH_3COO). *Benson* [24] has reported $\Delta H^\circ_{f(298)}$ for the radicals HCOO, HCO and CH_3CO to be approx. −36, +9.0 and −5.4 kcal/mol, respectively. An estimate for CH_3COO is obtained assuming the relationship

$$\Delta H^\circ_{f(298)}(CH_3COO) - \Delta H^\circ_{f(298)}(CH_3CO) = \Delta H^\circ_{f(298)}(HCOO) - \Delta H^\circ_{f(298)}(HCO)$$

This yields $\Delta H^\circ_{f(298)}(CH_3COO) = -50$ kcal/mol.

Another estimate is obtained using the (O,H)-bond strength D°_{298}:

$$CH_3COOH \rightarrow CH_3COO + H$$

$$D^\circ_{298}(CH_3COO{-}H) = 112(4) \text{ kcal/mol.}$$

This yields $\Delta H^\circ_{f(298)}(CH_3COO) = -44(4)$ kcal/mol.
In this work $\Delta H^\circ_{f(298)}(CH_3COO) = -50(5)$ kcal/mol is used.

Peracetoxy radical (CH_3COO_2). Assuming the approximation

$$\Delta H_{f(298)}(CH_3OOH) - \Delta H_{f(298)}(CH_3OO) = \Delta H_{f(298)}(CH_3COOOH) - \Delta H_{f(298)}(CH_3COO_2)$$

one finds from known data [24] $\Delta H_f(CH_3COO_2) \approx -41$ kcal/mol. Using the bond dissociation energy $D_0(HOO{-}H) \approx +90(2)$ kcal/mol one obtains the same value.

Acetyl nitrate (CH_3COONO_2). Methyl acetate and acetanhydride are compared to methyl nitrate and acetyl nitrate

$$CH_3OCOCH_3 \leftrightarrow CH_3(CO)OCOCH_3$$

$$CH_3ONO_2 \leftrightarrow CH_3(CO)ONO_2$$

It is assumed that the contribution to enthalpy of formation is equal if a carbonyl group is introduced either into methyl acetate or methyl nitrate:

$$\begin{aligned}\Delta H^\circ_{f(298)}&(CH_3(CO)OCOCH_3) - \Delta H^\circ_{f(298)}(CH_3OCOCH_3) =\\ &= \Delta H^\circ_{f(298)}(CH_3(CO)ONO_2) - \Delta H^\circ_{f(298)}(CH_3ONO_2),\end{aligned}$$

then

$$\Delta H^\circ_{f(298)}(CH_3COONO_2) \approx -72 \text{ kcal/mol.}$$

In this way it is attempted to include the effect of resonance energy which usually is attributed to the anhydride fragment (aliphatic). The value obtained from group contributions *(Benson)* yields −63 kcal/mol. However, no resonance energy is included.

Peroxyacetyl nitrate $(CH_3COO_2NO_2, PAN)$. The following compounds may be compared in analogy to CH_3COONO_2

$$(CH_3CO)_2O_2 \leftrightarrow (CH_3CO)_2O$$

$$(CH_3CO)(NO_2)O_2 \leftrightarrow (CH_3CO)(NO_2)O$$

yielding $\Delta H^\circ_{f(298)}(CH_3COO_2NO_2) \approx -59$ kcal/mol. This value is in good agreement with the estimates of *Cox et al.* [32] and *Domalski* [33] which are −57.7 and −57. 2 kcal/mol, respectively.

Formyl nitrate $(HCOONO_2)$, *peroxyformyl nitrate* $(HCOO_2NO_2)$. The same methods as above may be used for the estimates

$$\Delta H^\circ_f(HCOONO_2) \approx -52 \text{ kcal/mol}$$

$$\Delta H^\circ_f(HCOO_2NO_2) \approx -39 \text{ kcal/mol.}$$

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