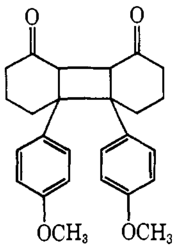
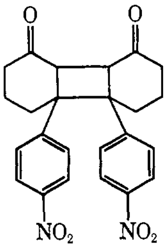
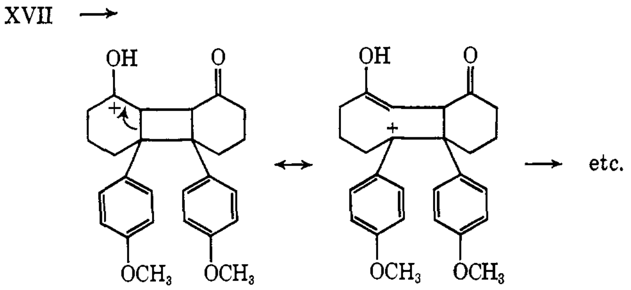

XVII


XVIII


XVIIa

XVIIb

readily to the ion at m/e 203 (65%) and this is undoubtedly due to the stabilization, by the *p*-anisyl group, of the resonance form XVIIb of the QM+ ion. Such stabilization is not present in the QM+ ion derived from XVIII.

The studies of the aliphatic photodimers demonstrate that it is possible to assign an h-h or h-t structure to an unknown photodimer from an examination of its methane CI spectrum. Clearly in correlations of this type factors such as an aromatic ring that significantly affect the stability of the carbonium ions must be taken into account in structural assignments.

Acknowledgments. We thank Dr. O. L. Chapman for samples of the isophorone photodimers and Dr. P. Yates for samples of XVII and XVIII.

Chemical Ionization Mass Spectrometry. XI. Reactions of Methoxymethyl Formate and Methoxymethyl Acetate with Methane and Isobutane

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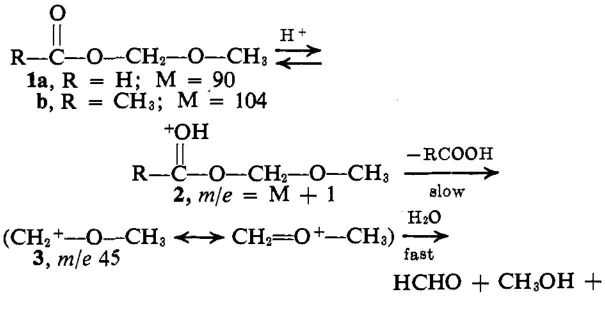
Abstract: The chemical ionization mass spectra of methoxymethyl formate and methoxymethyl acetate have been determined at several temperatures using isobutane and methane as reactants. The major ions observed in the isobutane spectra are the protonated molecule ions and an ion with *m/e* 101, which is formed by displacement of the carboxylic acid by *t*-butyl cation. No methoxymethyl cation is observed. In the methane spectra the methoxymethyl cation is by far the most abundant ion. Rate constants for its formation from the two esters were determined at several temperatures. At 300°K the rate constant for the formation of this ion from methoxymethyl formate is a factor of two higher than that for the formation of the ion from methoxymethyl acetate, which is in agreement with the relative rates found in solution. Activation energies and frequency factors are given, but the significance of the magnitudes obtained for these quantities is not understood.

Chemical ionization mass spectrometry[1] is a process wherein organic substances may be ionized by reaction with a set of reactant ions in the ionization chamber of a mass spectrometer. In many cases the reactions which are observed in these experiments are analogous to those which the organic substances undergo in acidic solution.[2,3]

The acid-catalyzed hydrolysis of simple partial acylals has been studied by Salomaa and his coworkers,[4] and that of more complex partial acylals by one of us.[5] Thus, it appeared that a study of the behavior of methoxymethyl formate (**1a**) and methoxymethyl acetate (**1b**) in the acidic plasmas generated in chemical ionization mass spectrometry would provide a comparison of the gaseous and solution phase chemistry of these simple partial acylals.

Methoxymethyl formate and methoxymethyl acetate undergo hydrolysis in aqueous acid by an $A_{Al}1$ mechanism[5] (eq 1). One would expect this mechanism to be



$$R{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}O{-}CH_3 \underset{}{\overset{H^+}{\rightleftarrows}}$$
1a, R = H; M = 90
b, R = CH$_3$; M = 104

$$R{-}\overset{^+OH}{\overset{\|}{C}}{-}O{-}CH_2{-}O{-}CH_3 \xrightarrow[\text{slow}]{-RCOOH} \quad (1)$$
2, *m/e* = M + 1

$$(CH_2{}^+{-}O{-}CH_3 \longleftrightarrow CH_2{=}O^+{-}CH_3) \xrightarrow[\text{fast}]{H_2O} HCHO + CH_3OH + H^+$$
3, *m/e* 45

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[1] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

[2] F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

[3] F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969).

[4] P. Salomaa, *Acta Chem. Scand.*, **11**, 132 (1957); **14**, 586 (1960).

[5] D. P. Weeks, A. Grodski, and R. Fanucci, *J. Amer. Chem. Soc.*, **90**, 4958 (1968); D. P. Weeks and G. W. Zuorick, *ibid.*, **91**, 477 (1969).

operative since unimolecular cleavage of the protonated substrate **2** would yield the inherently stable methoxymethyl cation (**3**). We believed that a similar protonation ionization leading to **3** would occur in the chemical ionization mass spectrometry experiment. In aqueous hydrochloric acid the formate **1a** hydrolyzes about 3 times faster than the acetate, **1b**. We hoped that chemical ionization mass spectrometry would show a similar pattern, *viz.*, that under the same conditions **1a** would be more extensively ionized to the methoxymethyl cation.

Results and Discussion

Isobutane as the Reactant Gas. The acid-catalyzed hydrolysis rates of **1a**, **1b**, and benzyl acetate are qualitatively similar. Previous work done by one of us[3] has shown that the acidic plasma formed by using isobutane as the reactant gas (mainly *t*-butyl cations) was sufficiently strong to protonate and cause considerable cleavage of benzyl acetate. Therefore, we began our experiments using isobutane as the reactant gas expecting the major process to lead to ions at *m/e* M + 1 (**2**) and *m/e* 45 (**3**).

Tables I and II give the chemical ionization mass spectra at several temperatures of methoxymethyl formate and methoxymethyl acetate using isobutane as the reactant gas. Somewhat contrary to our expectations, no ions are observed at *m/e* 45. Note that the highest temperature at which spectra were determined is about 100° lower in the formate compound. Higher temperature measurements on the formate were not undertaken because of the suspicion that the compound had a deleterious effect on the mass spectrometer.

Table I. Chemical Ionization Mass Spectra of Methoxymethyl Formate and Isobutane Reactant[a]

m/e	Ion	Relative intensity at *t* = 41°	87°	121°
61	$^+HHCO_2CH_3$		0.018	0.022
69	$CH_2\cdots C^+H\cdots C(CH_3)_2$	0.009	0.017	0.030
70	?	0.012	0.013	0.016
71	?	0.009	0.013	0.017
77	?	0.011	0.018	0.028
91	$^+HHCO_2CH_2OCH_3$	0.134	0.236	0.220
100	?	0.022	0.016	
101	$CH_2\text{-}O^+\text{-}CH_3$ | | $CH_2\text{-}C(CH_3)_2$	0.518	0.528	0.569
102	C^{13} isotope	0.039	0.035	0.049
103	?	0.036	0.013	
105	?	0.015	0.010	0.015
129	$(C_3H_3^+)HCO_2CH_2OCH_3$	0.023		
135	$HCO_2CH_2O^+(CH_2OCH_3)CH_3$	0.030	0.022	0.019
147	$HCO_2CH_2O^+(C_4H_9)CH_3$	0.100	0.035	0.014
148	C^{13} isotope	0.010		
Others of relative intensity <0.010		0.032	0.026	0.001

[a] $P_{i\text{-}C_4H_{10}} = 0.70$ Torr; $P_{HCO_2CH_2OCH_3} = 5 \times 10^{-5}$ Torr; mol wt = 90.

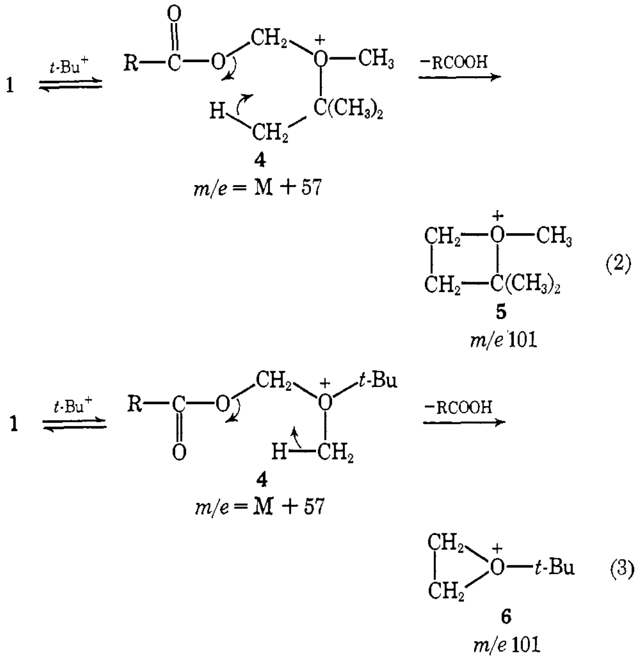
An unexpected feature of the spectra is the appearance of an ion at *m/e* 101, which constitutes the $(M + 11)^+$ ion from the formate ester and the $(M - 3)^+$ ion from the acetate ester. The intensities are large, greater than 50% of the additive ionization in the case of the formate. Scrutiny of these and other peaks in the spectra led us to conclude that the ion at *m/e* 101 could arise from **1** by initial formation of a complex between the *t*-butyl cation (acting as a Lewis acid) and the methoxy oxygen of the partial acylal. Indeed, this fragment is present in the spectrum of **1a**, appearing at *m/e* 147 $(M + 57)^+$. Proton transfer and the loss of formic acid would leave a fragment with mass M + 11 (actually M + (57 − 46)). This is illustrated in Scheme I. A similar process for **1b** would lead to the same ion $((M + 57) - 60))^+$.

Table II. Chemical Ionization Mass Spectra of Methoxymethyl Acetate and Isobutane Reactant[a]

m/e	Ion	Relative intensity at *t* = 46°	78°	151°	214°
69	$CH_2\cdots C^+H\cdots C(CH_3)_2$	0.008	0.010	0.032	0.055
71	?	0.006	0.008	0.012	0.012
75	$^+HAcOCH_3$			0.027	0.102
93	?	0.015	0.026	0.015	
101	$CH_2O^+CH_3$ | | $CH_2C(CH_3)_2$	0.123	0.137	0.143	0.157
102	C^{13} isotope	0.009	0.010	0.017	0.015
105	$^+HAcOCH_2OCH_3$	0.497	0.539	0.670	0.590
106	C^{13} isotope	0.027	0.029	0.037	0.038
143	$(C_2H_3^+)AcOCH_2OCH_3$	0.014	0.012		
149	$AcOCH_2O^+(CH_2OCH_3)CH_3$	0.197	0.152	0.046	0.019
150	C^{13} isotope	0.016	0.013		
209	$^+H(AcOCH_2OCH_3)_2$	0.024	0.010		
Others of relative intensity <0.010		0.064	0.054	0.001	0.012

[a] $P_{i\text{-}C_4H_{10}} = 0.70$ Torr; $P_{AcOCH_2OCH_3} = 5 \times 10^{-5}$ Torr; mol wt = 104.

Scheme I



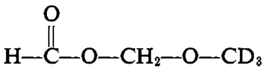
We considered that there were at least two reasonable pathways for the proton transfer which are shown in Scheme I as eq 2, a six-membered cyclic transition state, and eq 3, a five-membered cyclic transition state. We prepared and investigated trideuteriomethoxymethyl formate (**7**) in order to distinguish between eq 2 and 3 and also to aid in the assignment of other fragments which appear in the chemical ionization mass spectra of **1a** and **1b**. If the process illustrated in eq 2 is operating the trideuterated compound, **7** should yield an ion at *m/e* 104. If the path in eq 3 is important one should observe an ion at *m/e* 103. Table III contains the

Table III. Chemical Ionization Mass Spectra of Trideuteriomethoxymethyl Formate and Isobutane Reactant[a]

m/e	Ion	Relative intensity at t = 38°	77°	222°
69	$CH_2\stackrel{\cdots}{-}C^+H\stackrel{\cdots}{-}C(CH_3)_2$	0.009	0.011	0.117
70	?	0.010	0.014	
71	?	0.011	0.010	0.022
94	$^+HHCO_2CH_2OCD_3$	0.144	0.202	0.054
95	C^{13} isotope	0.008	0.010	
103	$\begin{array}{l}CH_2O^+CHD_2\\ \vert\quad\;\;\vert\\ CH_2C(CH_3)_2\end{array}$	0.049	0.041	0.030
104	$\begin{array}{l}CH_2O^+CD_3\\ \vert\quad\;\;\vert\\ CH_2C(CH_3)_2\end{array}$	0.447	0.510	0.649
105	?	0.040	0.036	0.054
106	?	0.033	0.025	0.036
108	?	0.046	0.017	0.020
141	$HCO_2CH_2O^+(CH_2OCD_3)CD_3$	0.013	0.016	
150	$HCO_2CH_2O^+(C_4H_9)CD_3$	0.106	0.055	
151	C^{13} isotope	0.011		
Others of relative intensity <0.010		0.073	0.053	0.018

[a] $P_{i-C_4H_{10}} = 0.70$ Torr; $P_{HCO_2CH_2OCD_3} = 5 \times 10^{-5}$ Torr; mol wt = 93.

chemical ionization mass spectrum of **7**. The ion which appears at m/e 104 having an intensity comparable with that of the ion at m/e 101 from **1a** strongly indicates that eq 2 is correct. A fragment does appear at m/e 103. However, its intensity is about that which would be predicted from the isotopic impurity (CHD_2OD) in the methanol-d_4 which was used to prepare **7**. Indeed, at comparable temperatures the sum of the intensities from the m/e 103 and m/e 104 ions in the spectrum of **7** is virtually equal to the intensity of the m/e 101 ion from **1a**.



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-O-CD_3$$

7

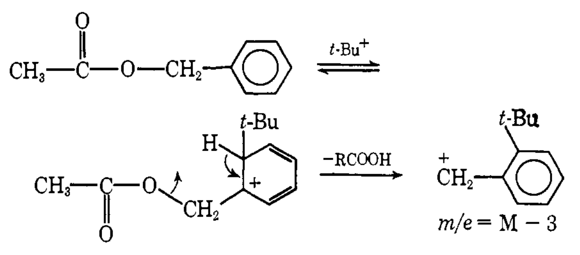
To provide further information about these reactions we have determined the mass spectrum of n-propyl acetate (Table IV), which is analogous to **1b** except that it does not contain the nucleophilic methoxy oxygen. No $(M - 3)^+$ ion is observed, which supports the postulate that a nucleophilic center in addition to the carbalkoxy group is needed to produce $(M - 3)^+$ ions.

Table IV. Chemical Ionization Mass Spectrum of n-Propyl Acetate and Isobutane Reactant[a]

m/e	Ion	Rel int[b]
101	$CH_3COOCHC_2H_5^+$	0.014
102	$CH_3COOC_3H_7^+$	0.015
103	$CH_3COOC_3H_7 \cdot H^+$	0.890
104	C^{13} isotope	0.062
205	$(CH_3COOC_3H_7)_2H^+$	0.019

[a] $P_{i-C_4H_{10}} = 0.70$; $P_{n-C_3H_7OAc} = 5 \times 10^{-5}$ Torr; source temperature = 106°; mol wt = 102. [b] Relative intensity.

This concept allows the identification of one of the unassigned fragments from the chemical ionization of benzyl acetate[3] and *para*-substituted benzyl acetates.[6] An $(M - 3)^+$ ion of low to moderate intensity appears for several of the benzyl acetates when isobutane is the reactant gas. In each case these ions correspond to $((M + 57) - 60)^+$ (eq 4) where the phenyl ring is serving as the nucleophilic center with which the t-butyl cation complexes.



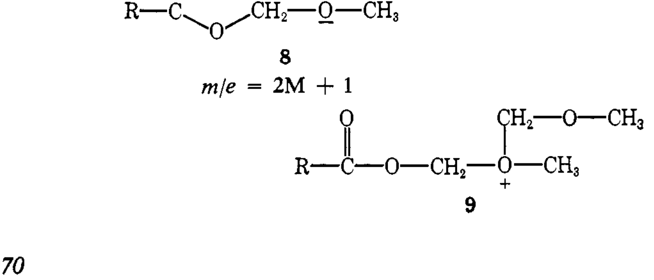
(4)

Careful consideration of these transformations shows that the data are self-consistent. The two formates, **1a** and **7**, yield high and about equal intensities of $(M + (57 - 46))^+$ (**5**). In addition, they each show a small but observable $(M + 57)^+$ ion (**4**). The acetate, **1b**, on the other hand, yields an $((M + 57) - 60)^+$ ion of much lower intensity. We believe that this difference is due to another route which competes with the formation of **4**, *viz.*, simple protonation of the substrate by the t-butyl cation acting as a Brønsted acid (*vide infra*). Since the acetate is more basic than the formate, one would expect, and one sees, more of the acetate going to the $(M + 1)^+$ ion and, therefore, less acetate being available for complexation with t-butyl cation. The $(M + 57)^+$ ion is not observed in the spectrum of the acetate. If we assume that the ratio of **4** to **5** for the acetate is about the same as that for the formates, then the amount of $(M + 57)^+$ (m/e 161) would be in the vicinity of 1% of the total ionization and, therefore, on the borderline of observable signals.

An ion of low intensity at m/e 69 appears in the spectra of **1a**, **1b**, and **7**. We believe that it is the 1,1-dimethylallyl cation.

We mentioned above that the alternative fate of the substrate ester was to suffer protonation yielding, initially, an $(M + 1)^+$ ion. The $(M + 1)^+$ ion appears in the spectra of all three compounds. We have observed that the acetate, **1b**, is more susceptible to simple protonation than the two formates **1a** and **7**. The fate of this ion was not entirely predictable. Thus, we have already noted the absence of the methoxymethyl cation (**3**). On the other hand, we did observe the formation of a familiar ion at $m/e = 2M + 1$ from methoxymethyl acetate. This "protonated dimer" appears in the chemical ionization mass spectra of benzyl acetates[3] and other esters.[1] There is good indirect evidence for the formation of the protonated dimer from methoxymethyl formate as well. Consider the process shown in Scheme II.

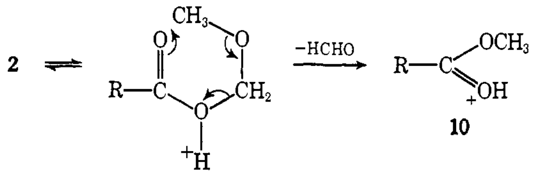
Scheme II



The ion of low intensity (2.4% of the total ionization) at *m/e* 209 in the spectrum of the acetate is the protonated dimer, **8b**. The corresponding ions for the formates at *m/e* 181 for **1a** and at *m/e* 189 for **7** were not observed. Subsequent loss of the carboxylic acid from **8** leads to **9**. Note the similarity between this pathway and the one in eq 2. The ion, **9**, appears in the spectra of all three compounds. The intensity of **9b** (*m/e* 149) is almost 20% of the total ionization at the lowest temperatures studied. On the other hand, **9a** (*m/e* 135) and the corresponding ion from **7** (*m/e* 141) represent less than 3% of the total ionization at a comparable temperature. This is almost certainly due to the paucity of the $(M + 1)^+$ ion from the formate. Thus, if we assume that the compounds will form about equal ratios of **8** and **9**, the amount of protonated dimer for the formate will be well below the 1% of total ionization necessary to be observed.

Finally, at higher temperatures in the spectrum of **1a** an ion at *m/e* 61 appears which we believe is protonated methyl formate (**10**). A possible pathway for the formation of **10** is shown in Scheme III. Protonated methyl acetate at *m/e* 75 is present in the spectrum of **1b** at higher temperatures. Formation of the protonated methyl esters has been observed in the chemical ionization of these partial acylals when methane was used as the reactant gas (*vide infra*). The migration which we propose is indicated by the presence of an ion at *m/e* 64 for the trideuterated material, **7**. When isobutane is used the ion at *m/e* 64 is not observed which conflicts with the proposal in Scheme III. Taking the evidence on balance we believe that Scheme III is correct.

Scheme III



The greater tendency observed in this work for the formate ester **1a** to form the $(M + 57)^+$ association complex with *t*-butyl cation and the greater tendency for the acetate ester **1b** to form the $(M + 1)^+$ ion by proton transfer from *t*-butyl cation are part of a general behavior pattern, the outlines of which are in the process of emerging. It appears that the tendency of the *t*-butyl cation to act as a Lewis acid to form the $(M + 57)^+$ association complex or as a Brønsted acid to form the $(M + 1)^+$ ion depends on the base strength of M and/or on the temperature. With low base strength and low temperature the $(M + 57)^+$ association complex is favored. Thus we have observed[6] that in *p*-nitrobenzyl acetate at low temperatures the dominant ion formed is $(M + 57)^+$, but in benzyl acetates with less electronegative substituents and in *p*-nitrobenzyl acetate at higher temperatures, the proton transfer process dominates. Base strength should be related to ionization potential, and while we do not know the ionization potentials of benzyl acetate and *p*-nitrobenzyl acetate, it is of interest that in methyl benzoate and *p*-nitromethyl benzoates (to which the same considerations should apply) the ionization potentials are 10, 20,[7] and 9.35 eV,[7] respectively. The ionization potentials of methoxymethyl formate and methoxymethyl acetate are not available, and we use methyl formate and methyl acetate to illustrate the relative basicities of the formate and acetate groups. The ionization potential of $HCOOCH_3$ is 10.815 eV[7] and that of CH_3COOCH_3 is 10.27 eV,[7] which suggests that a significant difference in the basicities of these groups should exist. The reactions with the *t*-butyl cation are compatible with this difference. Similar effects are observed in the reactions of the *t*-butyl cation with aliphatic alcohols and with thiomethoxymethyl acetate.[8]

Methane as the Reactant Gas. The discovery that isobutane reactant did not provide conditions sufficient for observing cleavage to methoxymethyl cation (**3**) led us to use methane as the source of acidic plasma (approximately equal amounts of CH_5^+ and $C_2H_5^+$).

Tables V–VII show that the chemical ionization

Table V. Chemical Ionization Mass Spectra of Methoxymethyl Formate and Methane Reactant[a]

m/e	Ion	Relative intensity at *t* = 58°	100°	156°
45	$^+CH_2OCH_3$	0.729	0.899	0.926
46	C^{13} isotope	0.029	0.021	0.024
47	$HCO_2H_2^+$	0.047		
61	$^+HHCO_2CH_3$	0.088	0.034	0.034
91	$^+HHCO_2CH_2OCH_3$	0.044	0.030	0.016
135	$HCO_2CH_2O^+(CH_2OCH_3)CH_3$	0.010	0.007	
Others of relative intensity <0.010		0.053	0.009	

[a] $P_{CH_4} = 1.00$ Torr; $P_{HCO_2CH_2OCH_3} = 5 \times 10^{-5}$ Torr; mol wt = 90.

Table VI. Chemical Ionization Mass Spectra of Methoxymethyl Acetate and Methane Reactant[a]

m/e	Ion	Relative intensity at *t* = 62°	124°	187°
37	?	0.022		0.024
45	$^+CH_2OCH_3$	0.721	0.761	0.827
46	C^{13} isotope	0.020	0.022	0.019
61	$AcOH_2^+$	0.054	0.061	0.037
73	$AcOCH_2^+$	0.037	0.029	0.027
75	$^+HAcOCH_3$	0.054	0.064	0.046
105	$^+HAcOCH_2OCH_3$	0.091	0.050	0.022
Others of relative intensity <0.010		0.001	0.013	

[a] $P_{CH_4} = 1.00$ Torr; $P_{AcOCH_2OCH_3} = 5 \times 10^{-5}$ Torr; mol wt = 104.

Table VII. Chemical Ionization Mass Spectrum of Trideuteriomethoxymethyl Formate and Methane Reactant[a]

m/e	Ion	Relative intensity
47	$^+CH_2OCHD_2$	0.061
48	$^+CH_2OCD_3$	0.831
49	C^{13} isotope	0.020
64	$^+HHCO_2CD_3$	0.068
94	$^+HHCO_2CH_2OCD_3$	0.013
Others		0.007

[a] $P_{CH_4} = 1.00$ Torr; $P_{HCO_2CH_2OCD_3} \simeq 5 \times 10^{-5}$ Torr; source temperature = 152°; mol wt = 93.

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(6) F. H. Field, submitted for publication.

(7) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Drake, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, Washington, D. C., 1969.

(8) Unpublished studies in this laboratory.

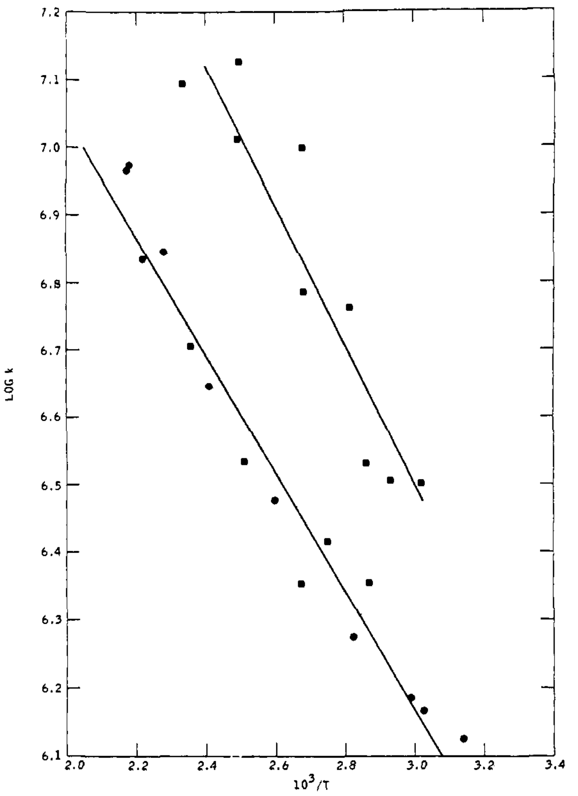


Figure 1. Log k *vs.* $1/T$ for: ●, $\mathrm{CH_3COOCH_2OCH_3{\cdot}H^+ \rightarrow CH_3COOH + CH_2OCH_3^+}$; ■, $\mathrm{HCOOCH_2OCH_3{\cdot}H^+ \rightarrow HCOOH + CH_2OCH_3^+}$.

mass spectra of **1a**, **1b**, and **7** contain only a few ions and that the methoxymethyl cation dominates the spectrum in each case. All the ionization observed can be accounted for by an initial protonation of the substrate to form $(M + 1)^+$. Loss of the carboxylic acid leads to **3** which appears at *m/e* 45 for **1a** or **1b** and *m/e* 48 for **7** (isotopic impurity results in an observable *m/e* 47 ion). In all cases this ion accounts for better than 70% of the total ionization. Thus, our original purpose of reproducing eq 1 in the gas phase has been accomplished.

There are several other ions of interest in the spectra when methane is the reactant gas. As with isobutane reactant, protonated methyl formate (**10a**) and protonated methyl acetate (**10b**) are observed and probably arise *via* the process in Scheme III. In these experiments the ion expected from **7** at *m/e* 64 is present. A small amount of the protonated carboxylic acid at *m/e* 47 or *m/e* 61 appears in these spectra. An ion at *m/e* 73 from the acetate **1b** may be the result of protonation on the methoxy oxygen and subsequent loss of methanol.

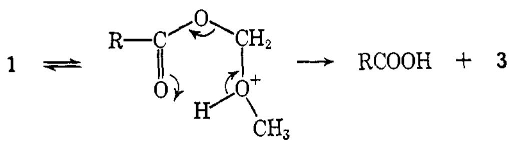
Temperature Effects. As may be seen from Tables V and VI the intensities of the $(M + 1)^+$ ions decrease with increasing temperature with a corresponding increase in the intensities of the $\mathrm{CH_2OCH_3^+}$ ions. We suggest that this is the consequence of increased rates of the decomposition of the protonated molecule ions (eq 5). Mass spectra of the two compounds were obtained at several ionization chamber temperatures, and using calculational techniques described previously,[3] rate constants for eq 5 were obtained. Arrhenius plots of the rate constants are given in Figure 1, and the kinetic constants obtained from these plots are given in Table VIII. The lines in the plots and the kinetic quantities are obtained from least-squares fits. The quantity k_{300} is the rate constant at 300°K.

$$\mathrm{RCOOCH_2OCH_3H^+ \longrightarrow RCOOH + CH_2OCH_3^+} \qquad (5)$$

Table VIII. Kinetic Parameters for Formation of $\mathrm{CH_2OCH_3^+}$

Compound	E_a (kcal/mol)	A (sec⁻¹)	k_{300} (sec⁻¹)
$\mathrm{HCOOCH_2OCH_3}$	4.8	4.5×10^9	1.4×10^6
$\mathrm{CH_3COOCH_2OCH_3}$	4.0	6.5×10^8	7.5×10^5

The most significant quantities are the values of k_{300}, and one sees that the rate constants for the two compounds differ by a factor of two with methoxymethyl formate having the higher value. In solution the methoxymethyl formate hydrolysis is faster by a factor of three,[4] and so the relative magnitudes of the rate constants in gas phase and in solution agree very well. The difference in the activation energies obtained in the present study is small, and the slower rate of decomposition of the protonated methoxymethyl acetate is primarily the result of a lower A factor. The E_a and A values obtained for the two compounds studied have unexpected values, and we are at present unable to assess the significance of the values observed. Indeed, both A factors are quite low compared with the values of 10^{12} observed previously[3,6] for the decomposition of some protonated acetates, and taken at face value this indicates that the entropies of activation for the compounds studied here are negative and rather large. An explanation of the low frequency factor may lie in a cyclic transition state. Thus, protonation of the methoxy group would lead to **11** which could decompose as shown.[9]



11

Experimental Section

The instrumentation and procedures of chemical ionization mass spectrometry have been described elsewhere.[3]

The partial acylals used in this study were all prepared by the reaction of sodium formate or sodium acetate with chloromethyl methyl ether or trideuteriomethyl chloromethyl ether.[10] The chloromethyl methyl ether was prepared by bubbling dry hydrogen chloride through a mixture of methanol and trioxymethylene.[10]

Methoxymethyl formate was prepared in 40% yield and fractionated through a 5-cm glass helix column; bp 103° (lit.[4] bp 103.6°); ir ($\mathrm{CHCl_3}$) 3020 ($\mathrm{O{-}CH_2{-}O}$), 2840 ($\mathrm{O{-}CH_3}$), and 1730 cm⁻¹ (C=O); nmr (10% $\mathrm{CDCl_3}$) δ 8.15 (s, 1), 5.34 (s, 2), and 3.50 ppm (s, 3).

Methoxymethyl acetate was prepared in 35% yield and fractionated: bp 117–118.5° (lit.[4] bp 118°); ir ($\mathrm{CHCl_3}$) 3030, 2850, and 1740 cm⁻¹; nmr (10% $\mathrm{CDCl_3}$) δ 5.12 (s, 2), 3.47 (s, 3), and 2.10 ppm (s, 3).

Trideuteriomethoxymethyl formate was prepared in 26% yield starting with methanol-d_4 (Stohler Isotope Chemicals, Inc.); bp 106°; ir ($\mathrm{CHCl_3}$) 3020, 2220, and 1725 cm⁻¹.

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(9) This explanation was suggested to us by a referee and also by Professor Mark Green of the University of Michigan.

(10) B. B. Allen and H. R. Henze, *J. Amer. Chem. Soc.*, **59**, 540 (1937); S. P. Lingo and H. R. Henze, *ibid.*, **61**, 1574 (1939).

Acknowledgment. The authors thank Mr. William Petersen of Esso for running the mass spectrometer and Mr. Steven Szucs of Seton Hall who prepared several of the compounds while working under a National Science Foundation institutional grant for undergraduate research.

Analysis of the Proton Nuclear Magnetic Resonance Spectra of Some Strained Benzocycloalkenes and Benzocycloalkenediones. Effect of Strain on Proton–Proton, Spin–Spin Coupling Constants[1]

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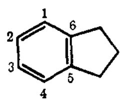
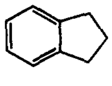
Abstract: The proton nmr spectra of some benzocycloalkenes and benzocycloalkenediones have been analyzed. The derived proton–proton spin–spin couplings have been examined for any features which might indicate partial bond fixation (the "Mills–Nixon effect") ascribable to ring strain in these series. Whereas the *ortho* couplings (^3J) exhibit no clear trends, it is found that the *meta* coupling (^4J) decreases sharply, and the *para* coupling (^5J) increases sharply with increased strain. The reasons for these changes are discussed in terms of empirical relationships found in other series, and also from a theoretical (extended Hückel molecular orbital) treatment.

Nearly 40 years ago Mills and Nixon suggested[3] that certain differences in the chemical reactivities of some indan and tetralin derivatives could be explained if the strain of fusing a five-membered ring onto the benzene nucleus caused partial fixation of the double bonds in the aromatic system. In line with the theory of aromaticity prevailing at that time they suggested that in indan the relative energies of the Kekulé structures[4] **1a** and **1b** were altered in favor of **1b**. Further experimental work[5] showed that the original chemical evidence was ambiguous, and a theoretical study[6] of the bond-length and bond-angle strains in indan showed that **1a** should be more favored, with fusion of a small alicyclic moiety serving to shorten bond 5–6 and lengthen bond 2–3.

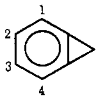


1a

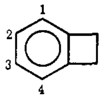


1b

Although the Mills–Nixon effect as originally proposed[3] has been disproved, the possibility of partial bond fixation and concomitant partial loss of aromatic character in benzocycloalkenes has continued to attract attention, and the smaller benzocycloalkenes, in particular, have recently received considerable study. Syntheses of benzocyclopropene,[7,8] **2**, and benzocyclobutene,[9] **3**, have been achieved, and there has been considerable discussion as to whether **2** is fully aromatic.[7,8,10] The only pertinent thermodynamic study[11] which has appeared interpreted the heat of hydrogenation of **3**, *viz.* −50.3 kcal/mol compared to a value of −47.3 kcal/mol for *o*-xylene, as illustrating "the smallness of the effect of strain on aromatic resonance." Moreover, from a discussion of the properties of *o*-di-*t*-butylbenzene, in which the strain energy has been estimated[12] by a variety of methods to be *ca.* 22 kcal/mol, a value much larger than that estimated for **3** (*ca.* 3–5 kcal/mol),[11] it has been suggested that "there is no evidence from nmr, infrared, or electronic spectra or from the reactions of compounds containing the *o*-di-*t*-butylbenzene system that a nonaromatic benzene has been pro-



2



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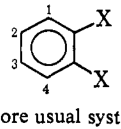
(1) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

(2) NASA Resident Research Associate, 1968–1970.

(3) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

(4) Since we shall refer both to Kekulé structures, and also to aromatic compounds where no specific bonding structure is implied, double bonds will only be used in the former case, and in the latter instance formally aromatic structures will be indicated thus

For clarity in the discussion the following numbering for *ortho*-disubstituted benzenes



will be used in place of the more usual system.

(5) See G. M. Badger, *Quart. Rev.* (London), **5**, 147 (1951).

(6) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **42**, 756 (1946).

(7) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964).

(8) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).

(9) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2255 (1958).

(10) E. F. Ullmann and E. Buncel, *ibid.*, **85**, 2106 (1963).

(11) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Colburn, and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

(12) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *ibid.*, **89**, 5389 (1967).