

THE EFFECT OF SUBSTITUENTS ON MASS SPECTRA OF ACETOXY(METHYL)SILANES  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$ \*G.DUBE<sup>a</sup>, U.PAPE<sup>a</sup> and V.CHVALOVSKÝ<sup>b</sup><sup>a</sup> Zentralinstitut für physikalische Chemie, Akademie der Wissenschaften der DDR, 1199 Berlin-Adlershof, DDR and<sup>b</sup> Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát 2

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A general scheme of fragmentation of the title compounds has been derived from their mass spectra: it consists of two competitive reaction sequences which are initiated by the cleavage of the methyl or acetoxy radical from the molecular ion. Primary fragmentation products decompose by these two reaction sequences releasing stepwise acetoxy groups from the central atom to form ketene and hydroxyl groups. From comparison of experimental intensities of the primary fragments with the values for a modified model system calculated according to the quasi-equilibrium theory of mass spectra, conclusions have been drawn concerning dissociation bond energies in the molecular ions of acetoxy(methyl)silanes: Si—C and Si—O bond energies are very low, the Si—O bond energy being always greater than the Si—C bond energy; the difference between dissociation energies of Si—C and Si—O bonds decreases with decreasing number of the methyl groups in the molecular ion. These substituent effects are interpreted.

## Mass Spectra

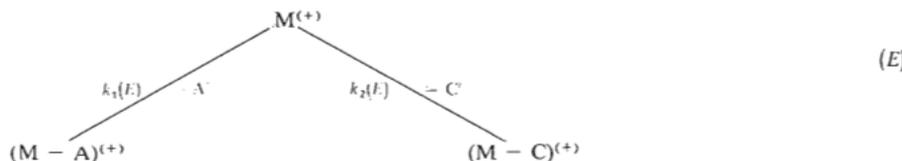
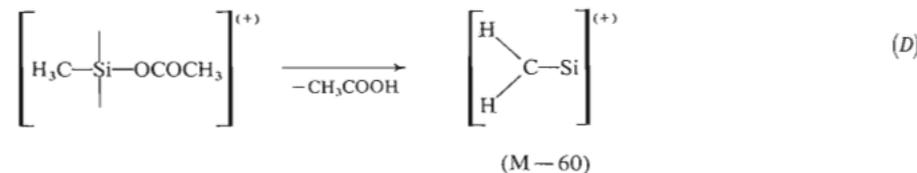
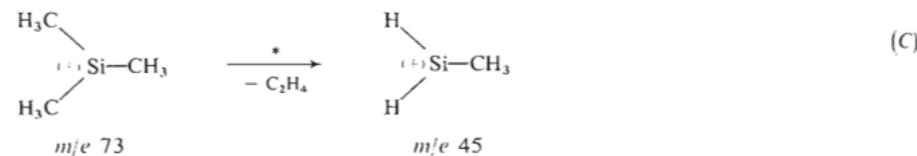
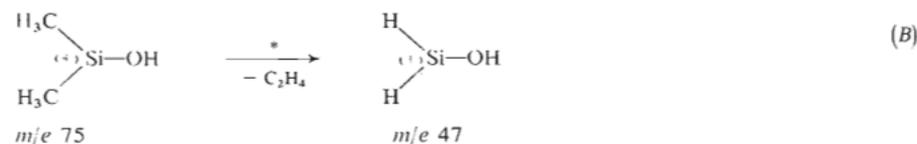
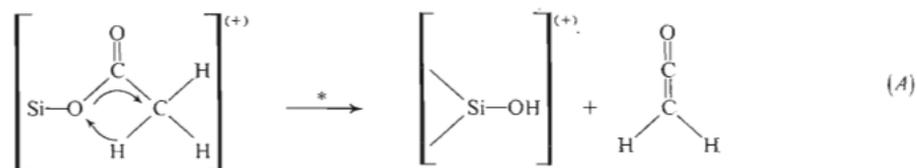
The spectra of the compounds  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$  ( $n = 0-3$ ) are shown in Fig. 1. In Table I are given the abundances of the ions present in each spectrum. These are related both to the intensity of the base peak (% *I*) (the base peak mass) and to the total current of ions (% *I*).

## Fragmentation Schemes

A general fragmentation scheme (Scheme 1) can be deduced from the mass spectra. It involves the most important steps of electron impact fragmentation and consists of two competitive reaction sequences. The first one (1) is initiated by the cleavage of the methyl radical from the molecular ion, the other (2) by the cleavage of the acetoxy radical. These primary fragmentations are followed by rearrangements which proceed in both reaction sequences essentially by the same mechanism; the transient formation of a four-center activated complex leads to ketene, and the acetoxy group is converted via hydrogen transfer into the hydroxyl group (Eq. (A)). Similar fragmentations have been already observed with halogenated phenyl acetates<sup>1</sup>

\* Part CLII in the series Organosilicon Compounds; Part CLI: This Journal 42, 1859 (1977).

and tert-butyl acetates<sup>2</sup>. These rearrangements speak for the occurrence of metastable ions in the mass spectra of acetoxy silanes. These ions are marked by star both in an example of the fragmentation (Scheme 1) and in the spectra (Fig. 1).



SCHEME 1

General Scheme of Fragmentation of the  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$  Compounds

TABLE I  
Mass Spectra of the  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$  Compounds ( $n = 0-3$ )

$m/e$	Intensity		$m/e$	Intensity	
	% $I(119)$	% $\Sigma I$		% $I(119)$	% $\Sigma I$
	$\text{CH}_3\text{Si}(\text{OCOCH}_3)_3$			$(\text{CH}_3)_2\text{Si}(\text{OCOCH}_3)_2$	
15	1.071	0.2844	14	1.743	0.4097
28	3.660	0.9715	15	7.059	1.660
42	3.125	0.8293	16	0.7778	0.1828
43	13.75	3.650	18	0.6078	0.1429
44	1.571	0.4171	26	1.268	0.2981
45	4.613	1.224	27	0.6536	0.1537
59	1.045	0.2773	28	13.72	3.226
60	1.768	0.4692	29	1.438	0.3380
61	0.7679	0.2038	41	0.7059	0.1659
62	0.9196	0.2440	42	4.575	1.076
63	1.768	0.4692	43	25.92	6.095
74	0.5625	0.1493	44	2.353	0.5531
76	5.624	1.493	45	16.56	3.892
77	40.47	10.74	46	1.157	0.2719
78	2.976	0.7898	47	4.226	0.9935
79	11.61	3.081	51	1.020	0.2397
80	0.6161	0.1635	58	0.6340	0.1490
81	0.5714	0.1517	59	2.919	0.6863
93	1.161	0.3081	60	3.507	0.8246
103	0.8661	0.2298	61	3.420	0.8041
118	7.589	2.015	62	1.294	0.3043
119	100.00	26.54	63	3.638	0.8553
120	9.375	2.448	73	0.5948	0.1398
121	56.24	14.93	74	6.078	1.429
122	4.107	1.090	75	44.44	10.45
123	2.738	0.7266	76	7.712	1.813
135	1.089	0.2891	77	72.55	17.05
136	2.113	0.5607	78	4.575	1.076
137	0.5357	0.1421	79	3.594	0.8451
160	15.45	4.100	91	0.9346	0.2197
161	50.89	13.50	103	0.6078	0.1429
162	6.101	1.620	116	14.81	3.483

TABLE I  
(Continued)

<i>m/e</i>	Intensity		<i>m/e</i>	Intensity	
	% <i>I</i> (119)	% $\Sigma I$		% <i>I</i> (119)	% $\Sigma I$
163	16.07	4.265	117	32.46	7.631
164	1.563	0.4147	118	4.379	1.029
165	0.7589	0.2015	119	100.00	23.51
178	1.589	0.4218	120	8.562	2.013
220(M)	—	—	121	4.641	1.091
			134	2.353	0.5530
			161	15.03	3.533
			162	1.547	0.3636
				0.7190	0.1690
			176(M)	0.5556	0.1306
	$(\text{CH}_3)_3\text{Si}(\text{OCOCH}_3)^a$			$\text{Si}(\text{OCOCH}_3)_4^b$	
14	0.5568	0.2362	14	0.9464	0.2741
15	2.811	1.193	15	3.750	1.086
26	0.7568	0.3211	28	5.922	1.715
27	0.5459	0.2316	32	0.8839	0.2560
28	3.892	1.652	42	4.761	1.379
29	1.766	0.7491	43	22.02	6.377
31	0.6703	0.2844	44	1.545	0.4473
42	1.639	0.6956	45	1.446	0.4189
43	9.568	4.059	60	0.8304	0.2405
44	1.603	0.6802	61	0.5714	0.1655
45	12.43	5.274	62	1.223	0.3542
46	0.9622	0.4082	63	1.232	0.3558
47	4.324	1.834	76	1.759	0.5094
51	0.5081	0.2156	78	0.6875	0.1992
55	0.5297	0.2247	79	19.94	5.775
58	0.9243	0.3921	80	1.491	0.4318
59	2.306	0.9784	81	1.61	0.3361
60	1.207	0.5121	92	0.6786	0.1965
61	4.162	1.766	103	0.5179	0.1499
72	1.099	0.4662	104	0.9018	0.2612
73	11.53	4.892	120	3.898	1.129

TABLE I  
(Continued)

<i>m/e</i>	Intensity		<i>m/e</i>	Intensity	
	% <i>I</i> (119)	% $\Sigma I$		% <i>I</i> (119)	$\Sigma I$
74	3.225	1.368	121	100.00	28.96
75	100.00	42.43	122	7.768	2.250
76	7.297	3.096	123	4.672	1.353
77	4.108	1.743	134	0.5446	0.1578
93	0.5676	0.2408	137	1.089	0.3155
117	50.81	21.56	138	1.018	0.2948
118	4.811	2.041	139	0.9196	0.2663
119	2.072	0.8790	162	2.708	0.7843
132(M)	—	—	163	74.11	21.46
			164	7.321	2.120
			165	3.631	1.052
			180	0.6071	0.1759
			204	0.8482	0.2457
			205	54.16	15.69
			206	6.429	1.862
			207	2.738	0.7929
			222	0.5536	0.1603
			264(M)	—	—

<sup>a</sup> % *I*(75), %  $\Sigma I$ ; <sup>b</sup> % *I*(121), %  $\Sigma I$ .

The number of reaction steps *z* depends in each sequence upon the number of methyl groups, *n*. In the reaction sequence 1 *z* for *n* = 0 is 0 and for *n* = 1–4 it is 5–*n*; in the reaction sequence 2 *z* for *n* = 1–4 is equal to 4–*n*.

In some cases the rearrangements involved in both competitive reaction sequences have been accompanied by further fragmentation reactions. By the action of electron impact upon  $(\text{CH}_3)_2\text{Si}(\text{OCOCH}_3)_2$  and  $(\text{CH}_3)_3\text{SiOCOCH}_3$ , the dimethylhydroxysilyl cation formed decomposes according to Eq. (B), and the trimethylsilyl cation, the primary product in fragmentation of  $(\text{CH}_3)_3\text{SiOCOCH}_3$ , undergoes further fragmentation according to Eq. (C).

These cleavage reactions have been already reported for electron impact fragmentation of other organosilicon compounds<sup>3–7</sup>.

During fragmentation of the compounds  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$  ( $n = 1, 2$ ) we have observed in addition to the sequences (1) and (2) also another fragmentation

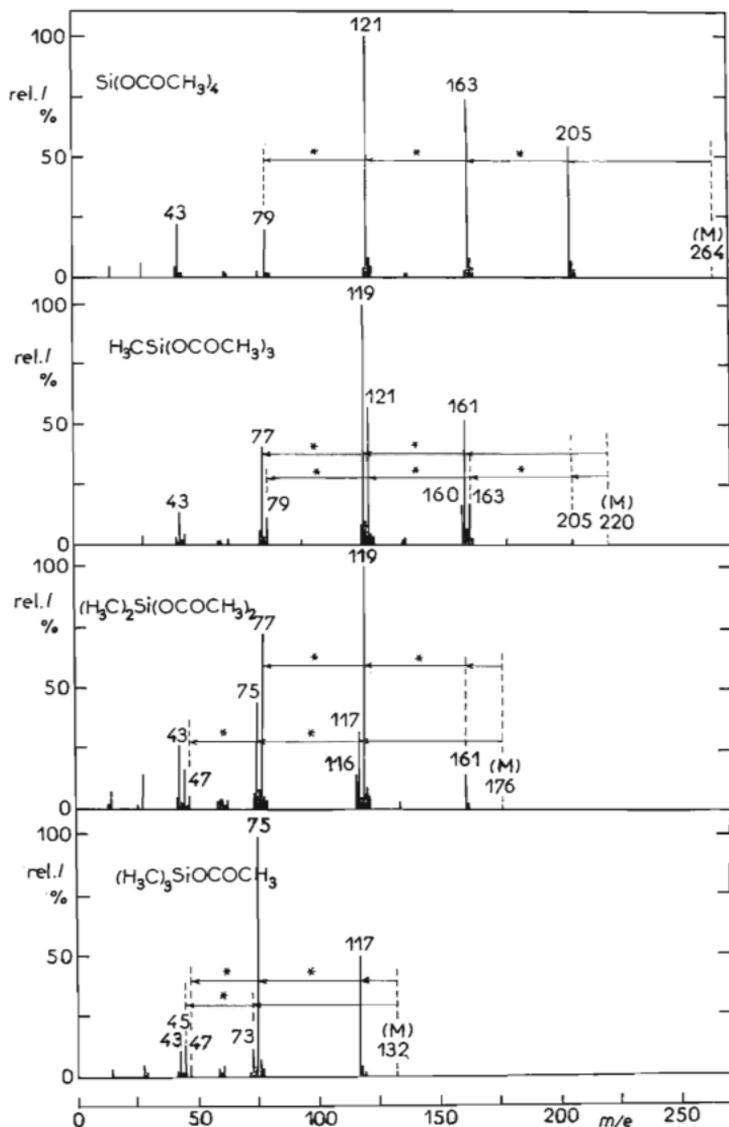


FIG. 1

Mass Spectra of the  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$  Compounds ( $n = 0-3$ )

path which originates from the displacement of the neutral molecule of acetic acid from the molecular ion (Eq. (D)).

This reaction is followed by elimination of ketene according to the mechanism already described. The number of reaction steps which start gradually from the (M-60) fragment equals to  $3-n$  for the above compounds. The intensity of the fragments of this sequence in the mass spectra is very low (Table II).

TABLE II

Calculated Intensities of the Peaks in the Mass Spectra of the  $A_nBC_{4-n}$  Compounds and Starting Values for Calculation

Series	Model	Values for $k_1, E$			Values for $k_2(E)$			Calculated intensities		
		$\beta_1 = n$	$E_{01}$ eV	$\frac{s-1}{2}$	$\beta_2 =$ $= (4-n)$	$E_{02}$ eV	$\frac{s-1}{2}$	$I(M)$	$I(M-A)$	$I(M-C)$
I	$ABC_3$	1		35.5	3		35.5	0.05	0.71	0.24
	$A_2BC_2$	2	1.00	31.0	2	1.00	31.0	0.04	0.48	0.48
	$A_3BC$	3		26.5	1		26.5	0.03	0.34	0.73
II	$ABC_3$	1		35.5	3		35.5	0.05	0.36	0.59
	$A_2BC_2$	2	1.00	31.0	2	1.10	31.0	0.04	0.60	0.36
	$A_2BC$	3		26.5	1		26.5	0.03	0.80	0.17
III	$ABC_3$	1		35.5	3		35.5	0.05	0.48	0.46
	$A_2BC_2$	2	1.00	31.0	2	1.20	31.0	0.04	0.69	0.26
	$A_3BC$	3		26.5	1		26.5	0.03	0.84	0.12
IV	$ABC_3$	1		35.5	3		35.5	0.05	0.59	0.35
	$A_2BC_2$	2	1.00	31.0	2	1.30	31.0	0.04	0.76	0.20
	$A_3BC$	3		26.5	1		26.5	0.03	0.87	0.91
V	$ABC_3$	1		35.5	3		35.5	0.05	0.74	0.21
	$A_2BC_2$	2	1.00	31.0	2	1.50	31.0	0.04	0.85	0.11
	$A_3BC$	3		26.5	1		26.5	0.03	0.91	0.05
VI	$ABC_3$	1		35.5	3		35.5	0.05	0.89	0.05
	$A_2BC_2$	2		31.0	2	2.00	31.0	0.04	0.93	0.03
	$A_3BC$	3		26.5	1		26.5	0.03	0.95	0.01
VII	$ABC_3$	1		35.5	3		35.5	0.04	0.48	0.48
	$A_2BC_2$	2	0.85	31.0	2	1.04	31.0	0.03	0.69	0.28
	$A_3BC$	3		26.5	1		26.5	0.02	0.85	0.13

### The Effect of Substituents on Silicon upon the Mass Spectra

The variation of substituents attached to silicon in the studied series of compounds reflects qualitatively in the mass spectra of these substances (Fig. 1). Furthermore, the substitution affects also the competition between the cleavage of the methyl and acetoxy radicals from the molecular ions and thus also the intensities of the peaks  $I(\text{M} - \text{CH}_3)$  and  $I(\text{M} - \text{OCOCH}_3)$  in the mass spectra. In order to estimate these quantities it is necessary, of course, to take into account that the primary fragments undergo further fragmentations, as shown in Scheme 1. We have therefore determined the sums of the fragments formed according to the reaction sequence 1 and according to the sequence 2 and taken them as representative values for the intensities of the primary fragmentation products  $I(\text{M} - \text{CH}_3) = \sum I$  (the reaction sequence 1) and  $I(\text{M} - \text{OCOCH}_3) = \sum I$  (the sequence 2). To neglect the effect of other fragmentations in discussion of substituent effects, these values were further normalized such that the sum of  $I(\text{M} - \text{CH}_3)$  and  $I(\text{M} - \text{OCOCH}_3)$  equaled to one. These normalized intensities are further denoted as  $I'(\text{M} - \text{CH}_3)$  and  $I'(\text{M} - \text{OCOCH}_3)$ . Because of their low intensity, the molecular peaks have not to be considered in the above normalization. In Fig. 2 are represented graphically the dependences of  $I'(\text{M} - 15)$  and  $I'(\text{M} - \text{OCOCH}_3)$  values on the number of the methyl groups,  $n$ , in the compounds  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$ . The graph shows the data for tetramethylsilane whose main electron impact fragmentation reaction consists, according to literature data<sup>3,8</sup>, of the cleavage of the methyl radical from the molecular ion.

Interpretation of substituent effects have been aimed especially at estimating dissociation energies of  $\text{Si}-\text{CH}_3$  and  $\text{Si}-\text{OCOCH}_3$  bonds and their changes in the series of the compounds  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$  from their mass spectra. No doubt, electron impact fragmentation depends upon activation energies of fragmentation reactions; these represent dissociation energies of the bond which is to be cleaved

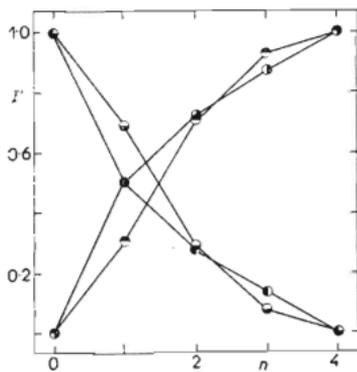


FIG. 2  
Experimental and Normalized Intensities of Fragments  $I'(\text{M} - \text{CH}_3)$  (●) and  $I'(\text{M} - \text{OCOCH}_3)$  (○) in the  $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$  System in Dependence upon  $n$  and their Comparison with Calculated (Table II, series VII) and Normalized Intensities  $I'(\text{M} - \text{A})$  (●) and  $I'(\text{M} - \text{C})$  (●) in the  $\text{A}_n\text{BC}_4-n$  System.

during electron impact fragmentation of molecular ions or of their fragments. The spectra thus allow to estimate only the dissociation energies of the bonds in the ions. These quantities are usually available directly from mass spectrometric measurements of the ionisation and appearance potentials. Such a possibility does not exist for the series of the compounds under study, since both molecular ions and fragmentation ions formed in the first step of the fragmentation exhibit so low intensity in the mass spectra that determination of ionisation or appearance potentials is either very inaccurate or quite impossible. The exception is  $(\text{CH}_3)_2\text{Si}(\text{OCOCH}_3)_2$  in which case the appearance potential of the  $(\text{M} - \text{CH}_3)^+$  and  $(\text{M} - \text{OCOCH}_3)^+$  fragments has been determined with satisfactory accuracy. When speaking about bonding in methylacetoxysilanes we are thus entirely dependent upon the intensities of the peaks in the mass spectra. The difficulty stems from the fact that these quantities are not determined only by the activation energies of fragmentation reactions but also by a number of other factors. These factors are either unknown for the series studied or their effects upon the intensity of the peaks is not clean-cut. These facts make an accurate evaluation of bond dissociation energies in the molecular ions of methylacetoxysilanes impossible. The explanation of substituent effects in the mass spectra of these compounds given further must be considered therefore only as an attempt at interpretation. We have proceeded in the following way: the intensities of the peaks were calculated according to the quasi-equilibrium theory of mass spectra for the system of model compounds of the general formula  $\text{A}_n\text{BC}_{4-n}$  which is adapted to the system studied. By comparison of the experimental intensities with calculated ones we attempted to obtain at least qualitative information about bonding in methylacetoxysilanes.

In the case of the  $\text{A}_n\text{BC}_{4-n}$  system the molecular ions decompose through two competition reactions (Eq. (E)).

The intensities of the molecular ions  $I(\text{M})$  and of fragment ions  $I(\text{M}-\text{A})$  and  $I(\text{M}-\text{C})$  were calculated according to the quasi-equilibrium theory of mass spectra whose applicability to the studied compounds can be expected. This theory<sup>9,10</sup> yields the expression (I) for the rate constants of fragmentation reactions induced by electron impact:

$$k(E) = \beta \nu \left( \frac{E - E_0}{E} \right)^s - 1, \quad (I)$$

where  $\beta$  is the number of the bonds of the same kind in an ion that is cleaved during a given fragmentation;  $\nu$  is the frequency factor,  $E$  is the internal energy of ions;  $E_0$  is the activation energy of fragmentation reaction = the dissociation energy of the cleavage of a given bond in the ion;  $s$  is the number of vibrational degrees of freedom for the ion.

Using usual kinetic equations for first order reactions we obtain the expressions

(2)–(4) for the intensity of the  $(\text{M} - \text{A})^+$  and  $(\text{M} - \text{C})^+$  ion fragments and the molecular ion  $\text{M}^+$  in the mass spectrum

$$I(\text{M} - \text{A}) = \int_{E_{01}}^{E_{\max}} f(E) \frac{k_1(E)}{k_1(E) + k_2(E)} (1 - \exp[-k_1(E)t_1 - k_2(E)t_1]) dE \quad (2)$$

$$I(\text{M} - \text{C}) = \int_{E_{02}}^{E_{\max}} f(E) \frac{k_2(E)}{k_2(E) + k_1(E)} (1 - \exp[-k_2(E)t_1 - k_1(E)t_1]) dE \quad (3)$$

$$I(\text{M}) = \int_0^{E_{01}} f(E) dE + \int_{E_{01}}^{E_{\max}} f(E) \exp(-k_1(E)t_2 - k_2(E)t_2) dE, \quad (4)$$

where  $f(E)$  is the energy distribution function;  $E_{\max}$  is the maximal internal energy of molecular ions,  $E_{01}$ ,  $E_{02}$  are activation energies for reactions (1) and (2), respectively;  $k_1(E)$ ,  $k_2(E)$  are the rate functions of reactions 1 and 2;  $t_1$  is the time of retention of ions in ionizing source;  $t_2$  is the time of the flight of the ions until their leave of the magnetic field in the mass spectrometer.

By such a calculation of the intensities we have intended to determine the effect of variation in the number of substituents A and C upon the intensities of the peaks of compounds  $\text{A}_n\text{BC}_{4-n}$ . The number of substituents A and C reflects in Eq. (5) the factor and the number of oscillators  $s$  at different values of  $E_{01}$  and  $E_{02}$ , all the other parameters being constant. We have used constant values for quantities  $f(E)$ ,  $v$  and  $t$  in calculations of the intensities according to Eqs (2)–(4). The energy distribution function used consists of two linear equations which for the same purpose were already used<sup>11,12</sup> in the general form (5).

$$f(E) = REE_{\max}^{-2} + SE_{\max}^{-1}. \quad (5)$$

In the following two equations (6) and (7)

$$f(E) = 6.67EE_{\max}^{-2} \quad (0 \leq E \leq 0.30E_{\max}) \quad (6)$$

$$f(E) = -2.86EE_{\max}^{-2} + 2.86E_{\max}^{-1} \quad (0.30E_{\max} \leq E \leq E_{\max}) \quad (7)$$

a value of 20 eV has been used in all cases for the maximal internal energy of molecular ions. On using the above constants for  $S$  and  $R$  the expression

$$\int_0^{E_{\max}} f(E) dE$$

acquires a value of 1. The frequency factors of competitive reactions 1 and 2 were taken as having the same value  $\nu_1 = \nu_2 = 1.00 \cdot 10^{13} \text{ s}^{-1}$ . The reaction times  $t$  for the mass spectrometer used by us were  $t_1 = 9 \cdot 10^{-7} \text{ s}$ ,  $t_2 = 1.11 \cdot 10^{-5} \text{ s}$ . The starting variables used in the calculation are summarized in Table II. The number of "effective oscillators"  $(s - 1)/2$  has been substituted for the exponent of the expression given by Eq. (1). To adapt this model to the system of methylacetoxysilanes we adopted a four atomic substituent A and a seven atomic substituent C.

The values of the intensities  $I(M)$ ,  $I(M - A)$ , and  $I(M - C)$  calculated according to Eqs (2)–(4) are presented in Table II. It is seen that low intensities of the molecular ions in the mass spectra of methylacetoxysilanes can be obtained only when the activation energy  $E_{01}$  and  $E_{02}$  are regarded as very low. From this it can be concluded – as the first information about bonding in methylacetoxysilanes – that the dissociation energies of the Si–CH<sub>3</sub> and Si–OCOCH<sub>3</sub> bonds in the molecular ions of these compounds has to be very low.

To compare the calculated values of the intensities  $I(M - A)$  and  $I(M - C)$  presented in Table II with experimental data for methylacetoxysilanes, which are represented graphically in Fig. 2, the sum of  $I(M - A)$  and  $I(M - C)$  was further normalized to a value of 1. The normalized intensities  $I'(M - A)$  so obtained are shown in Fig. 4. The values obtained with the same pairs of the values for  $E_{01}$  and  $E_{02}$  (series I–VI) were combined. The curves obtained show the dependence of the intensity of the  $(M - A)^+$  fragment in the  $A_nBC_{4-n}$  system upon the number  $n$ , all the other parameters determining the intensity of peaks in the mass spectrum being constant.

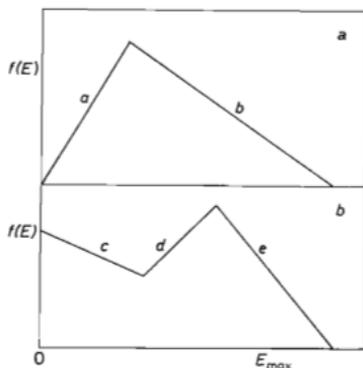


FIG. 3

Energy Distribution Function Used in Calculations of Intensities of the Peaks

3a) a: Eq. (6), b: Eq. (7); 3b) c: Eq. (8), d: Eq. (9), e: Eq. (10).

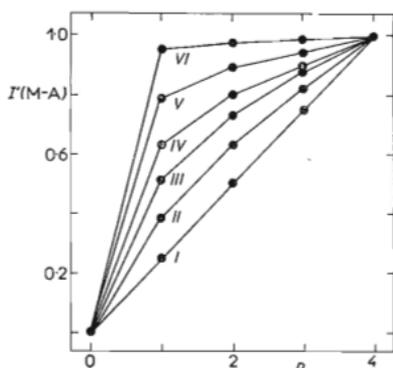


FIG. 4

Calculated and Normalized Intensities  $I'(M - A)$  in the  $A_nBC_{4-n}$  System in Dependence upon  $n$  (series I–VI, Table II)

As follows from comparison of Figs 2 and 4, the curve representing the experimental  $I'(\text{M} - \text{CH}_3)$  values is closest to the curve of the intensities  $I'(\text{M} - \text{A})$  found for the series III. From this it can be concluded – as the second information about bonding in methylacetoxy silanes – that the molecular ions of the compounds with  $n = 1 - 3$  have dissociation energies of the  $\text{Si}-\text{CH}_3$  bonds rather than those of the  $\text{Si}-\text{OCOCH}_3$  bonds. This information is in harmony with experimentally available data for the appearance potentials of the  $(\text{M} - \text{CH}_3)^+$  and  $(\text{M} - \text{OCOCH}_3)^+$  fragments in  $(\text{CH}_3)_2\text{Si}(\text{OCOCH}_3)_2$ , which are  $10.65 \pm 0.1$  eV and  $10.84 \pm 0.1$  eV, respectively. If we accept, in accordance with this, a value of 0.85 eV and of 1.04 eV for the dissociation energy of the  $\text{Si}-\text{CH}_3$  or  $\text{Si}-\text{OCOCH}_3$  bond in the molecular ion of this compound (Table II, series VII), we obtain a satisfactory agreement between calculated intensities and experimental data when for calculation the data applied to the determination of energy distribution function, frequency factor, the number of oscillators, and the time of flight for model compounds are used. If we calculate the intensities using the same pair of values of activation energies also for  $\text{CH}_3\text{Si}(\text{OCOCH}_3)_3$  and  $(\text{CH}_3)_3\text{SiOCOCH}_3$  (Table II, series VII), we obtain too high or too low value for the intensity of the  $I'(\text{M} - \text{CH}_3)$  peak, as evident from Fig. 2.

The reason for this discrepancy can be looked for in that this calculation has been made without considering changes in the energy distribution function, frequency factors and activation energies which could be connected with the change in  $n$ . To describe the effect of changes in these quantities upon the intensities of the peaks, we had to perform further calculations.

TABLE III

Comparison of the Intensities Calculated by Using Different Energy Distributions and then Normalized with Experimental Data

Model	Energy distribution $f(E)$ for calculation	Calculated and normalized intensities		Experimental and normalized intensities	
		$I'(\text{M} - \text{A})$	$I'(\text{M} - \text{C})$	$I'(\text{M} - \text{CH}_3)$	$I'(\text{M} - \text{OCOCH}_3)$
$\text{ABC}_3$	eqs (12)–(14)	0.48	0.53	0.31	0.69
$\text{A}_2\text{BC}_2$		0.70	0.30	0.71	0.29
$\text{A}_3\text{BC}$		0.86	0.14	0.93	0.07
$\text{ABC}_3$	eqs (10), (11)	0.50	0.50	0.31	0.69
$\text{A}_2\text{BC}_2$		0.72	0.28	0.71	0.29
$\text{A}_3\text{BC}$		0.87	0.13	0.93	0.07

First of all, we calculated once more the intensities obtained in the series VII using a significantly changed function of energy distribution. Such a modified function  $f(E)$  is shown in Fig. 3b. It consists of three linear equations (8)–(10).

$$f(E) = -1.65EE_{\max}^{-2} + 1.35E_{\max}^{-1} \quad (0 \leq E \leq 0.35E_{\max}) \quad (8)$$

$$f(E) = 3.47EE_{\max}^{-2} + -0.44E_{\max}^{-1} \quad (0.35E_{\max} \leq E \leq 0.60E_{\max}) \quad (9)$$

$$F(E) = -4.10EE_{\max}^{-2} + 4.10E_{\max}^{-1} \quad (0.60E_{\max} \leq E \leq E_{\max}). \quad (10)$$

The results obtained by these calculations are presented in Table III and compared both with experimental intensities and with the calculated energy distribution used originally. It is seen that the significant change in the energy distribution function leads to only slight changes in the values of  $I'(M - A)$  and  $I'(M - C)$ . The differences found between calculated and experimental intensities are not therefore caused by the change in the function of energy distribution which in the series of compounds under study could have been due to the change in  $n$ .

We have recalculated further the value of the intensities obtained in the series VII with changed frequency factors  $\nu_1$  and  $\nu_2$ . The results summarized in Table IV show that for the model compounds  $ABC_3$  and  $A_3BC$  the agreement between the calculated and experimental values of intensities can be obtained if we change the frequency factor  $\nu_1$  for compound  $ABC_3$  by  $6.00 \cdot 10^{-2} \text{ s}^{-1} = 200 \text{ cm}^{-1}$  and the frequency factor  $\nu_2$  for compound  $A_3BC$  by  $5.00 \cdot 10^{12} \text{ s}^{-1} = 167 \text{ cm}^{-1}$ . With regard to the results of the IR spectroscopic study of neutral molecules of this system<sup>13</sup> it seems unlikely that changes in  $n$  in the series of methylacetoxysilanes would be accompanied by such a drastic change in frequency factors.

TABLE IV

The Effect of Variation of Frequency Factors  $\nu_1$  and  $\nu_2$  for Model Compounds  $ABC_3$  and  $A_3BC$

Model	Frequency factor		Calculated and normalized intensities		Experimental and normalized intensities	
	$\nu_1$ $\text{s}^{-1}$	$\nu_2$ $\text{s}^{-1}$	$I'(M - A)$	$I'(M - C)$	$I'(M - \text{CH}_3)$	$I'(M - \text{OCOCH}_3)$
$ABC_3$	$4.00 \cdot 10^{12}$	$1.00 \cdot 10^{13}$	0.31	0.69	0.31	0.69
$A_2BC_2$	$1.00 \cdot 10^{13}$	$1.00 \cdot 10^{13}$	0.72	0.28	0.71	0.29
$A_3BC$	$1.00 \cdot 10^{13}$	$5.00 \cdot 10^{12}$	0.93	0.07	0.93	0.07

The results of intensity calculations indicate that the deviation of the calculated intensities from those experimentally found for model compounds  $\text{ABC}_3$  and  $\text{A}_3\text{BC}$  (Fig. 2) is caused by the values of the activation energies  $E_{01}$  and  $E_{02}$  used in the calculation. It is clear that these quantities for methylacetoxy silanes vary with the number of methyl groups in the molecular ion. The agreement between experimental intensities of the fragments and the values calculated for model compounds  $\text{ABC}_3$  and  $\text{A}_3\text{BC}$  can be obtained by using the values of activation energies  $E_{01}$  and  $E_{02}$  listed in Table V. With respect to the presumptions adopted, the absolute values of the activation energies used for calculation are not sufficient for interpretation. On the other hand, information concerning the trend in these values is justified: the following expression holds for differences in the activation energies  $\Delta E_0 = (E_{02} - E_{01})$ :

$$\Delta E_0(\text{ABC}_3) < \Delta E_0(\text{A}_2\text{BC}_2) < \Delta E_0(\text{A}_3\text{BC}) .$$

As the third information about bonding in methylacetoxy silanes it can be deduced that in the molecular ions of the compounds containing one to three methyl groups, the difference between the dissociation energy of the  $\text{Si}-\text{OCOCH}_3$  and  $\text{Si}-\text{CH}_3$  bond decreases with decreasing number of methyl groups.

#### Interpretation of Substituent Effects

Comparison of experimental intensities with calculated intensities of the peaks of fragments in the mass spectra of acetoxy silanes renders it possible to speak qualitatively about bonding in the molecular ions of these compounds. 1) Formation of ion fragments from the molecular ions of methylacetoxy silanes is accompanied

TABLE V

The Effect of Variation of Activation Energies  $E_{01}$  and  $E_{02}$  for Model Compounds  $\text{ABC}_3$  and  $\text{A}_3\text{BC}$

Model	Activation energy		Calculated and normalized intensities		Experimental and normalized intensities	
	$E_{01}$ eV	$E_{02}$ eV	$I'(M - A)$	$I'(M - C)$	$I'(M - \text{CH}_3)$	$I'(M - \text{OCOCH}_3)$
$\text{ABC}_3$	1.09	1.14	0.31	0.69	0.31	0.69
$\text{A}_2\text{BC}_2$	0.85	1.04	0.72	0.28	0.71	0.29
$\text{A}_3\text{BC}$	0.52	0.94	0.93	0.07	0.93	0.07

by a change in silicon atom hybridization from  $sp^3$  to  $sp^2$  (ref.<sup>7</sup>). The increase in the  $s$ -character of Si- $\sigma$ -orbitals leads to flattening of the fragment ion and an increase in disorder energy. As bond dissociation energy represents a change between the energy consumed by the cleavage of the corresponding bond and that released by reorganization of the fragment, rehybridization of the silicon atom during fragmentation is conditioned by bond dissociation energy decrease. Bond dissociation energies of the molecular ions of acetoxysilanes are therefore very low. 2)  $s$ -Character of  $\sigma$ -bonds of silicon atom in the fragment ions of methylacetoxysilanes depends upon the electronegativity of its bonding partners. In fragment ions with strongly electronegative substituents attached to the central atom, the  $\sigma$ -bonds of silicon exhibit low  $s$ -character. During fragmentation of such compounds the above rehybridization of silicon atom is taking place only to a small extent and bond dissociation energies are thus comparatively high. For that reason, the replacement of methyl groups in methylacetoxysilanes by electronegative acetoxy groups results in an increase in the dissociation energy of both Si—C and Si—O bonds. 3) Changes in the substitution of silicon atom affect not only the ion which is the product of a given fragmentation, but also bonding in the molecular ion. If bonding partners of silicon are substituents with  $\pi$ -electrons or free electron pairs, the latter share partially the positive charge of the molecular ion. By this their electronegativity increases. This is accompanied by a decrease in the  $s$ -character of  $\sigma$ -bonds between silicon and these partners, and also by a decrease in the energy required for the cleavage of these bonds. On the other hand, the  $s$ -character of  $\sigma$ -bonds of silicon with less electronegative bonding partners is increased, and the energy needed for the cleavage of these bonds increases. However, this effect compensates the influence described in paragraph 2 only to a limited extent. In the system of compounds studied the acetoxy group is the substituent which in the molecular ions of methylacetoxysilanes partially shares positive charge. Therefore, with increasing substitution of methyl groups for acetoxy groups the Si—C bond dissociation energy increases more than the Si—O bond energy.

## EXPERIMENTAL

Preparation and characterization of compounds used was reported earlier<sup>13</sup>. The spectra were recorded on a simple focusing mass spectrometer. Energy of electrons was 70 eV, ionizing source temperature was 250°C. Methylacetoxysilanes were introduced through an indirect inlet system at 150°C, tetraacetoxysilane directly at 20°C.

Appearance potentials of the primary fragments of dimethyldiacetoxysilane were determined by measuring the partial ion streams of fragments in dependence upon the energy of electrons and by treating semilogarithmically the curves obtained<sup>14</sup>. Intensities of the peak in the mass spectra of model compounds were calculated according to Eqs (2)–(4).

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