MASS-SPECTROMETRIC STUDY OF 1,3-OXAZACYCLOPENTANES

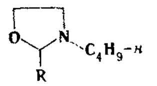
V. I. Kadentsev, R. A. Karakhanov,
I. A. Borisova, V. V. Zorin,
V. D. Sokovykh, T. V. Ivanova,
S. S. Zlot-skii, O. S. Chizhov,
and D. L. Rakhmankulov

UDC 543.51:541.63:547.787

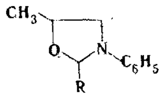
The fragmentation of 1,3-oxazolidines under electron-impact and chemical-ionization (with methane as the gas reagent) conditions and the effect of the substituent in the 2 position of the heteroring on the stability of the molecular ions (M^+) and on the character of the fragmentation of 1,3-oxazolidines were studied. It is shown that splitting out of an alkyl group from the 2 position is characteristic for electron impact. Processes involving alkylation and protonation with the formation of cluster ions are most characteristic for chemical ionization. In analogy with hydrolysis in the condensed phase, protonated 1,3-oxazolidine molecules split out an aldehyde molecule.

1,3-Oxazacyclopentanes are of definite interest from the point of view of the creation from them of corrosion inhibitors, extractants of precious metals, additives for oils and polymers, and biologically active preparations.

Data from a mass-spectrometric study of 1,3-oxazolidines I-V by means of electron impact (EI) and chemical ionization (CI) are discussed in this paper.



I-III



IV, V

I R=H; II, IV R=C_2H_5; III, V R=C_3H_7-iso

Molecular-ion peaks, the stability of which depends to a significant extent on the character of substituent R and decreases on passing from I to II and III and from IV to V, which is evidently associated with the stability of the radical that is split out, are observed in the EI mass spectra of all of the investigated compounds (Table 1). As expected, phenyl-substituted 1,3-oxazolidines IV and V display greater stability with respect to EI than their N-butyl analogs II and III.

One of the principal pathways of fragmentation of the molecular ions (M^+) of II-V is splitting out of an alkyl radical from the 2 position of the heteroring (Schemes 1 and 2), which leads to the appearance of relatively stable F_1 and F_2 ions with m/e 128 and 162, respectively.* The formation of such ions is characteristic for the fragmentation of 1,3-dioxolanes [1] and 1,3-dithianes [2]. Under electron impact the subsequent fragmentation of the F_1 and F_2 ions is determined by the substituent attached to the nitrogen atom. Thus in the case of butyl derivatives I-III one observes the preferred elimination of a molecule of butylene, and processes associated with cleavage of the oxazoline ring take place only to a very small degree (Table 1). In the case of phenyl derivatives IV and V fragmentation of the F_2 ions is accompanied by ring opening, which leads primarily to the formation of $[F_2 - CO]^+$, $[F_2 - CH_3CHO]^+$, and $HCNC_6H_5^+$ (F_3) ions. It is apparent from Table 1 that the contribution of these ions to the total ion current is considerably greater in the case of

---

*Here and subsequently in the text and in the schemes the numbers that characterize the ions are the mass-to-charge ratios.

Ufa Petroleum Institute, Ufa 450062. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1031-1034, August, 1981. Original article submitted April 16, 1980; revision submitted October 14, 1980.

TABLE 1. m/e Values and Relative Intensities (in percent of the maximum peak) of the Ion Peaks in the Electron Impact Mass Spectra of I-V

Arbitrary designation of the ion	I	II	III	IV	V
	M 129	*M* 157	*M* 171	*M* 191	*M* 205
M^+	129 (8,3)	157 (0,4)	171 (0,6)	191 (20,0)	205 (6,3)
[M–H]	128 (4,9)	157 (0,8)	170 (0,8)	190 (0,9)	204 (0,7)
F	128* (4,9)	128 (47,0)	128 (100,0)	162 (100,0)	162 (100,0)
F_1	84 (1,5)	84 (6,9)	84 (4,9)	104 (25,7)	104 (13,7)
F_2	57 (7,7)	57 (23,8)	57 (15,2)	77 (31,4)	77 (23,8)
F_3	100 (1,2)	100 (2,5)	100 (0,6)	134 (57,0)	134 (52,5)
F_4	— —	— —	— —	92 (4,0)	92 (3,4)
F_5	72 (7,7)	72 (100,0)	72 (63,7)	— —	— —
F_6	98 (1,2)	98 (5,3)	98 (5,4)	118 (6,9)	118 (5,8)
F_7	86 (100,0)	114 (5,0)	128* (100,0)	— —	— —
F_8	56 (22,4)	84* (6,9)	98* (5,4)	— —	— —
F_9	98* (1,2)	98* (5,3)	98 (5,4)	132 (6,9)	132 (5,8)
	87 (5,7)	68 (31,0)	56 (11,3)	91 (9,7)	135 (5,8)
	42 (3,5)	58 (40,3)	44 (28,4)	51 (11,1)	106 (5,6)
	29 (4,1)	56 (47,0)	43 (8,8)	29 (6,9)	91 (6,4)
		44 (50,0)	42 (12,8)		65 (6,1)
		42 (16,6)	41 (26,0)		
		41 (43,7)	29 (25,5)		

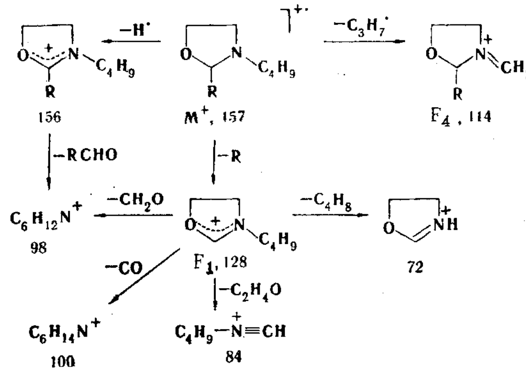
---

*The peak with the given m/e value corresponds to several isomeric ions.

IV and V than for derivatives I-III. It should be noted that the elimination of an R radical from M^+ and a CO molecule from the F_2 ions in the mass spectra of IV and V is accompanied by metastable transitions. Fragmentation of the amine type [3], which leads to the formation of F_4 ions (Scheme 1), is characteristic for the M^+ ions of alkyl derivatives I-III. This fragmentation pathway makes it possible to determine the alkyl substituent attached to the nitrogen atom. The formation of F_3 ions and the subsequent elimination of HCN molecules from the F_3 ions (the elimination of HCN molecules in the spectra of IV and V is also confirmed by the peaks of metastable ions), as a result of which F_5 ions are formed, give information regarding the aromatic substituent in derivatives IV and V.

It is apparent from Table 1 that the common pathway of fragmentation of the M^+ ions of all of the investigated compounds is the formation of $[M - H]^+$ fragment ions, which are characteristic for amines [3].

Scheme 1



Processes involving protonation and charge exchange [4], which lead to the formation of protonated molecular ions (MH^+) (the maximum peaks in the spectra), take place in the chemical ionization (CI) of I-V (Table 2) with methane as the gas reagent. Processes involving alkylation of the substrate molecules by the ions formed as a result of ion-molecular reactions during electron bombardment of the gas reagent also play a significant role under CI conditions, as indicated by the high intensities of the peaks of the $[M + C_2H_5]^+$ and $[M + C_3H_5]^+$ cluster ions. The latter make it possible to accurately record the MH^+ ions of the compounds in their spectra. One's attention is directed to the presence in the CI spectra of the investigated compounds of two groups of fragments. The first group is associated with fragmentation of the molecular ions. One should note above all that the M^+

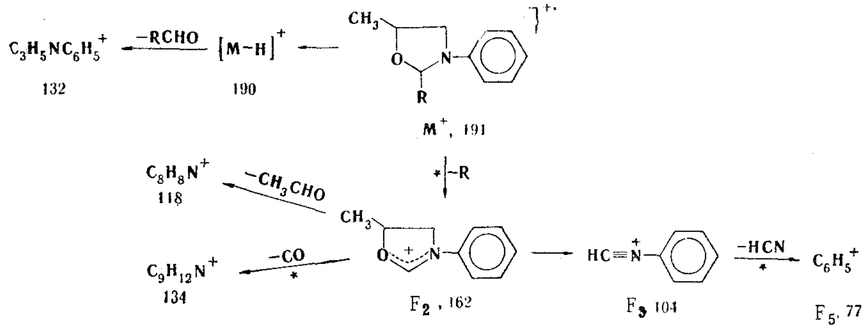
TABLE 2. m/e Values and Relative Intensities (in percent of the maximum peak) of the Ion Peaks in the Chemical-Ionization Spectra (with CH_4 as the gas reagent) of I-V

Ions	I	II	III	IV	V
	M 129	*M* 157	*M* 171	*M* 191	*M* 205
$[M+C_3H_5]^+$	170 (3,0)	198 (2,3)	212 (1,6)	232 (1,2)	246 (1,1)
$[M+C_2H_5]^+$	158 (12,5)	186 (14,4)	202 (11,1)	220 (12,8)	234 (13,0)
MH^+	130 (100,0)	158 (100,0)	172 (100,0)	192 (100,0)	206 (100,0)
M^+	129 (7,0)	157 (7,0)	171 (8,0)	191 (42,0)	205 (50,2)
$[MH-H_2]^+$	128 (23,2)	156 (30,0)	170 (32,4)	190 (14,6)	204 (19,2)
$[MH-CH_4]^+$	114 (4,0)	142 (5,7)	156 (9,4)	176 (2,1)	190 (5,0)
$[M-R]^+$	128* (23,2)	128 (35,4)	128 (67,0)	162 (29,0)	162 (39,4)
$[MH-RCHO]^+$	100 (4,3)	100 (20,6)	100 (31,7)	134 (18,2)	134 (13,4)
$[M-C_3H_7]^+$	86 (23,2)	114 (8,4)	128* (67,0)	— —	— —
$[M-R, -CO]^+$	100* (4,3)	100 (20,6)	100* (31,7)	162* (29,0)	162* (39,4)

*The peak with the given m/e value corresponds to several isomeric ions.

ions of I-V that are formed during chemical ionization are more stable and consequently less excited than the analogous ions that are formed under electron impact.

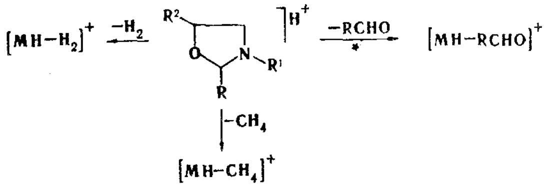
Scheme 2



Fragmentation of the M^+ ions leads to $[M-R]^+$ and $[M-C_3H_7]^+$ ions (for I-III) and $[M-R, -CO]^+$ ions (in the CI spectrum of V elimination of a CO molecule from the $[M-R]^+$ ion was confirmed by the corresponding metastable peak), which makes it possible to obtain information regarding both the R^1 (I-III) and R (I-V) substituents.

The second group of ions that are formed in the chemical ionization of I-V is associated with fragmentation of MH^+. This pertains primarily to the $[MH-H_2]^+$ ions [the M^+, $[MH-CH_4]^+$ (see [5] for evidence for the presence of alkyl substituents in the molecule), and $[MH-RCHO]^+$ ions make certain contributions to the intensity of the peak corresponding to this ion (Scheme 3)]:

Scheme 3



The ability of MH^+ to eliminate an aldehyde molecule (in the mass spectra of IV and V this reaction was confirmed by the corresponding metastable peaks) indicates an analogy between the processes involved in the fragmentation of the MH^+ ions of the protonated molecules in the gas phase and hydrolysis in a condensed medium [6], in which 1,3-oxazolidine undergoes decomposition to the corresponding aldehyde and amino alcohol.

One's attention is directed to the fact that the MH^+ ions of alkyl derivatives II and III are more inclined to eliminate an aldehyde molecule than the corresponding phenyl derivatives. This is apparently associated with the ability of the latter to undergo protonation in the phenyl group, as a result of which MH^+ ions that are not capable of undergoing fragmentation are formed.

Thus the CI spectra of the investigated compounds make it possible to easily identify the alkyl groups in the 1 and 2 positions of the heteroring, simplify the task of determining the molecular weights of substances, and make it possible to evaluate the effect of substituents attached to the N and C_2 atoms on the rate constant for the fragmentation of MH^+, which is of value for the study of the hydrolysis of these compounds. However, if the substituent attached to the nitrogen atom is an aryl group, the application of chemical ionization does not give unambiguous information regarding its structure, and in this case a combination of the EI and CI methods is most fruitful.

EXPERIMENTAL

Starting 1,3-oxazolidines I-V were obtained by the method in [6] by the reaction of amino alcohols with aldehydes and were purified by rectification with a column. The purity of I-V was monitored by chromatography and IR spectrometry (from the absence of absorption of C=O, HO, and NH groups). The purity of the samples was no lower than 99%.

The EI mass spectra were measured with a Varian chromatographic mass spectrometer at an ionizing voltage of 70 eV. The CI spectra were measured with a modified MKh-1303 mass spectrometer [7]. The spectra were recorded at a CH_4 gas reagent pressure of 0.6 torr, an ionization chamber temperature of 100°C, an ionizing-electron energy of 400 eV, and a cathode emission current of 50 μA. A specially developed system for introduction of the samples that consisted of a glass cylinder with a chromatographic inlet and a fine-regulation valve was used. The samples were heated to 100°C.

LITERATURE CITED

1. J. H. Beynon, Mass Spectrometry and Its Application to Organic Chemistry, Elsevier, Amsterdam (1960), pp. 368-369.
2. D. C. Jongh, J. Am. Chem. Soc., 86, 4027 (1964).
3. R. S. Gohlke and F. W. McLafferty, Anal. Chem., 34, 1281 (1962).
4. A. A. Solov'ev, V. I. Kadentsev, and O. S. Chizhov, Usp. Khim., 48, 7 (1979).
5. M. S. B. Munson and F. H. Field, J. Am. Chem. Soc., 89, 1047 (1967).
6. E. D. Bergmann, Chem. Rev., 53, 309 (1953).
7. A. A. Solov'ev, V. I. Kadentsev, O. S. Chizhov, D. N. Bel'kind, and A. G. Savel'ev, Prib. Tekh. Éksp., No. 2, 223 (1976).