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Primary Photoionisation Processes and Ion-Molecule Reactions in Organic Compounds

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This review deals with studies on primary photoionisation and molecular decomposition processes and ion-molecule reactions in the gas phase. Problems concerning the nature of the electronic and vibrational states arising on photoionisation and their role in unimolecular and bimolecular reactions of organic compounds are discussed.
Various pathways for the formation of secondary products in ion-molecule reactions have been determined. Data are presented on the energy relations of ion-molecule reactions and the proton affinities of molecules.
The bibliography includes 69 references.

CONTENTS

I.	Introduction	789
II.	Photoionisation and ion-molecule reactions in simple molecular and noble gases	790
III.	Ion-molecule reactions in saturated and unsaturated hydrocarbons	792
IV.	Photoionisation and ion-molecule reactions in ketones and alcohols	794
V.	Ion-molecule reactions in aromatic hydrocarbons	798
VI.	Proton affinity of molecules	798

I. INTRODUCTION

During recent years a new field has developed in the photochemistry of organic compounds—the photochemistry of gaseous ions, considering the elementary photoionisation processes and ion–molecule reactions (IMR) involving the ions formed on photoionisation. The development and application of the mass-spectrometric photoionisation method[1-3] yielded information about the excited and electronic states of radical-cations and the role of these states in the unimolecular decomposition reactions of the radical-cations into cations and radicals. The use of the appearance potentials of fragment ions made it possible to determine the heats of formation of cations of different structures and to refine the heats of formation obtained earlier by the electron impact method.

The data thus obtained on the electronic states and heats of formation of ions made it possible to consider the problem of the mechanisms and the pathways of ion–molecule reactions, which play an important role in high-energy chemistry and in the two-quantum photochemistry of organic compounds[4]. In the first place this concerns the elucidation of the role of the excitation of primary ions in ion–molecule reactions with the aim of investigating the mechanism by which the energy of the colliding species is redistributed. In the second place, for the study of the mechanism of ion–molecule reactions, it is important to know the different pathways for the formation of secondary ions and radicals both by hydrogen atom transfer from various groups of the molecule to the radical-cation and as a result of the involvement in the reactions of primary fragment ions. In the third place the elucidation of the way in which molecular properties such as basicity and polarisability influence the nature of ion–molecule reactions is very important.

In the present review these problems are considered in the discussion of studies on photoionisation and ion–molecule reactions occurring in the photoionisation of simple molecules and organic compounds—saturated and unsaturated hydrocarbons, aromatic hydrocarbons, aromatic compounds with heteroatoms, and aromatic hydrocarbons.

The studies on ion–molecule reactions by the electron impact methods have been reviewed[5-7]. The review of Tal'rose and Karachevtsev[5] deals with the study of ion–molecule reactions by the so called method of "internal" ionisation of molecules by electrons (the method of pulse withdrawal of ions). This method was first developed and applied by Tal'rose and Frankevich to measure the rate constants for ion–molecule reactions[8,9] and also to determine the proton affinities of molecules[10,11]. In subsequent studies the method of pulse withdrawal of ions was successfully employed in investigations of the mechanism of ion–molecule reactions involving thermal ions.

Important information about ion–molecule reactions was obtained by applying methods which permit the determination of the kinetic energies of ions produced in the reactions. The deflecting field method was used to determine the average kinetic energies of secondary ions and yielded information about the redistribution of the energy of the colliding species in ion–molecule reactions among the internal and translational degrees of freedom[12,13]. Measurement of the product energies for ion–molecule reactions by determining the changes in the momenta of secondary ions compared with the momentum which the primary ion receives when the molecule is ionised by an electron yielded data on the mechanism of ion–molecule reactions[14].

We may note that other aspects of ion–molecule reactions have also been elucidated[6,7,15]: the dependence of the cross-sections on the kinetic energy of the ions, angular distribution of products, etc.

Ion–molecule reactions in simple systems have been examined theoretically in studies on bimolecular gas-phase reactions[16,17]. It has been shown that ion–molecule reactions proceed via two pathways[16], namely via an intermediate complex mechanism and via a direct mechanism involving the "scission" of an ion from the incident species or the "capture" of a neutral species by the incident ion.

II. PHOTOIONISATION AND ION–MOLECULE REACTIONS IN SIMPLE MOLECULAR AND NOBLE GASES

1. Hydrogen

The ion–molecule reactions which occur on photoionisation of hydrogen were first investigated by Chupka et al.[3], who showed that the formation of the secondary H_3^+ ions involves the participation both of molecular hydrogen ions H_2^+ and excited hydrogen atoms. The primary molecular hydrogen ions H_2^+ were obtained in various excited vibrational states when hydrogen molecules were acted upon by monochromatic radiation (the energy spread was 0.002–0.05 eV) (Fig. 1):

$$H_2\,(X^1\Sigma_g^+,\ v''=0)+h\nu \rightarrow H_2^+\,(^2\Sigma_g,\ v'\geqslant 0)+e\,. \qquad (1)$$

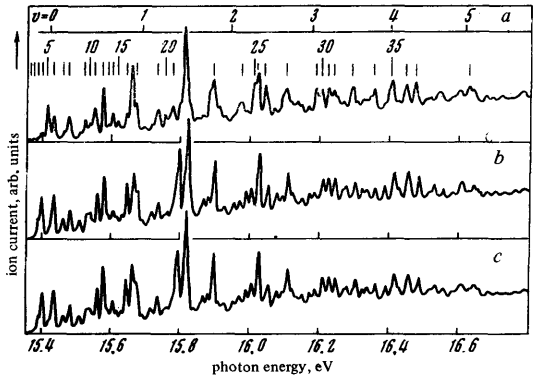


Figure 1. Appearance curves for H_2^+ and H_3^+ ions recorded with a resolution of 0.4 Å: *a*) H_2^+ from normal hydrogen; *b*) H_2^+ from parahydrogen; *c*) H_3^+ from parahydrogen.

Hydrogen atoms in the excited metastable state 2*S* were formed as a result of the predissociation of hydrogen molecules in the excited electronic state $D^1\Pi_u$:

$$H_2\,(X^1\Sigma_g^+,\ v''=0)+h\nu \rightarrow H_2\,(D^1\Pi_u,\ v'\geqslant 3) \rightarrow H_2\,(B^1\Sigma_u^+) \rightarrow H\,(1S)+H\,(2S)\,. \qquad (2)$$

This predissociation region of hydrogen molecules converges to a threshold of 14.66 eV. At the predissociation threshold the hydrogen atoms in the 2*S* state are formed with thermal kinetic energy, while for photon energies of 14.77 and 15.01 eV the hydrogen atoms in the 2*S* state are mainly produced as a result of the deactivation of hydrogen molecules in the excited vibrational states $v = 3$ and $v = 4$ respectively. The kinetic energies of the metastable hydrogen atoms corresponding to photon energies of 14.77 and 15.01 eV have been shown to be[18] 0.18 and 0.27 eV.

The cross-section of an ion–molecule reaction involving molecular hydrogen ions in the ground and excited vibrational states (Fig. 2),

$$H_2^+\,(^2\Sigma_g,\ v'\geqslant 0)+H_2\,(X^1\Sigma_g^+,\ v''=0) \rightarrow H_3^+ + H\,(1S)\,, \qquad (3)$$

decreases by 15–20% with increase of photon energy from the hydrogen ionisation potential (15.425 eV) to 16.6 eV. A decrease of the cross-section of reaction (3) with increasing vibrational excitation of the molecular ions H_2^+, i.e. with increase of the vibrational quantum number v from 0 to 5 is observed for kinetic energies of the primary ions less than 2 eV (laboratory system).

Studies on ion–molecule reactions in hydrogen on a double mass-spectrometer[19] showed that H_3^+ ions are formed via two pathways: both via proton and hydrogen atom transfer. With increase of the kinetic energy of molecular hydrogen ions from 1 eV upwards, the contribution of the process involving hydrogen atom transfer to the formation of secondary H_3^+ ions increases. For these kinetic energies of the molecular ions, both processes involve a direct mechanism, since their cross-sections are independent of the vibrational excitation energy of the molecular ions and the cross-section of the proton transfer process actually increases with increasing vibrational excitation of H_2^+ to 2 eV. For kinetic energies close to thermal energies, the proton transfer process contributes significantly to the formation of H_3^+ ions.

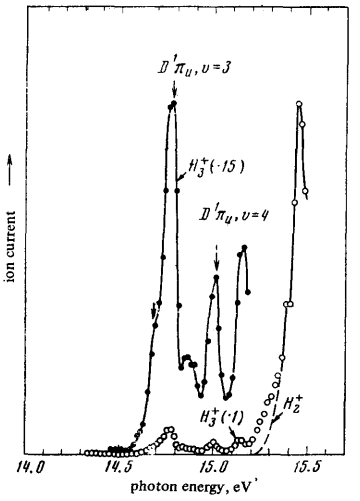


Figure 2. Appearance curves for H_2^+ and H_3^+ ions in the chemi-ionisation region recorded with a resolution of 2.5 Å. The arrow indicates the dissociation threshold of the hydrogen molecule (14.66 eV).

Fig. 2 shows that, in the range of photon energies below the hydrogen ionisation potential, the formation of H_3^+ ions involves the reaction of metastable hydrogen atoms with hydrogen molecules:

$$H\,(2S)+H_2\,(X^1\Sigma_g^+,\ v''=0) \rightarrow H_3^+ + e\,. \qquad (4)$$

Reaction (4) is exothermic, since at the predissociation threshold of the hydrogen molecule (14.66 eV) it involves metastable hydrogen atoms with thermal velocities. This finding serves as a basis for the determination of the heat of formation of H_3^+ ions:

$$\Delta H_f[H_3^+] \leqslant \Delta H_f[H\,(2S)] = 12.455\ \text{eV},$$

which corresponds to the lower limit of the proton affinity of the hydrogen molecule (3.396 eV).

On passing to photon energies of 14.77 and 15.01 eV, for which metastable hydrogen atoms are formed with an excess kinetic energy, the cross-section of reaction (4) has been shown[18] to decrease as v^{-n}, where v is the

velocity of the hydrogen atom and $n = 2-3$. In the range of photon energies between 15.20 eV and the hydrogen ionisation potential (15.425 eV), the observed increase of the yield of secondary H_3^+ ions must be attributed to reactions involving electronically excited hydrogen molecules:

$$H_2^* + H_2 (X^1\Sigma_g^+, v'' = 0) \rightarrow H_3^+ + H^- , \quad (5)$$

$$H_2^* + H_2 (X^1\Sigma_g^+, v'' = 0) \rightarrow H_3^+ + H(1S) + e . \quad (6)$$

It is important to note here that the contribution of reaction (4) to the formation of H_3^+ ions in this range of energies is insignificant for the reason indicated above. It has been shown[20] that highly excited long-lived states of the hydrogen molecule with a principal quantum number $n > 5$ play a significant role in reactions (5) and (6). The energies of such states lie in the region 0.1–0.2 eV below the ionisation potential of the hydrogen molecule.

2. Hydrogen and Noble Gases

The studies on the ion–molecule reactions observed in the ionisation of hydrogen molecules and noble gases by electron impact have dealt mainly with the identification of the reaction products and the investigation of the dependence of their cross-sections on the kinetic energies of the colliding species[21-25]. The ion–molecule reactions occurring on photoionisation of hydrogen molecules and helium, neon, and argon atoms and leading to the formation of the ions HeH^+, NeH^+, and ArH^+ have been investigated[26]. It has been shown that the formation of the HeH^+ and NeH^+ ions is associated with the involvement in the ion–molecule reactions of thermal molecular hydrogen ions in excited vibrational states:

$$H_2^+ (^2\Sigma_g, v' \geqslant 3) + He \rightarrow HeH^+ + H , \quad (7)$$

$$H_2^+ (^2\Sigma_g, v' \geqslant 2) + Ne \rightarrow NeH^+ + H . \quad (8)$$

Reactions (7) and (8) are observed for photon energies in excess of 16.20 and 15.97 eV, which corresponds to the formation of secondary HeH^+ and NeH^+ ions from vibrationally excited H_2^+ ions with quantum numbers $v \geqslant 3$ and $v \geqslant 2$ respectively. It has also been shown[26] that the cross-sections of ion–molecule reactions (7) and (8) increase with the vibrational excitation energy of the primary ions.

The formation of HeH^+ and NeH^+ ions involving hydrogen ions in the ground vibrational state is also observed, but in this case the ion–molecule reactions occur at the threshold of the kinetic energy of the initial H_2^+ ions[27].

On the basis of the foregoing data, one may conclude that the ion–molecule reactions leading to the formation of HeH^+ and NeH^+ ions proceed via an intermediate "complex", which ensures a redistribution of the internal and translational energy of the colliding species. It must be noted that the data obtained[26,27] on the role of excited vibrational states of molecules in ion–molecule reactions in hydrogen and noble gases are consistent with the results of the above electron impact studies.

On the basis of the photon energy thresholds for reactions (7) and (8), which are 16.20 and 15.97 eV, it is possible to determine the proton affinities of helium and neon. For helium, this quantity is 1.835 eV, while the proton affinity of neon determined from the energy threshold for reaction (8) is 2.08 eV. This value is consistent with the proton affinity of 2.15 ± 0.3 eV obtained by the electron impact method[21].

Ion–molecule reactions leading to the appearance of ArH^+ ions on photon ionisation of hydrogen and argon are exothermic, since they involve the primary H_2^+ and Ar^+ ions in both ground and excited states:

$$H_2^+ (^2\Sigma_g, v' \geqslant 0) + Ar \rightarrow ArH^+ + H , \quad (9)$$

$$Ar^+ (^2P_{3/2}, \text{ or } ^2P_{1/2}) + H_2 \rightarrow ArH^+ + H . \quad (10)$$

With increase of the photon energy from the hydrogen ionisation potential (15.425 eV) upwards, the cross-section of reaction (9) hardly changes, i.e. it is independent of the energy of the vibrational excitation of the initial molecular hydrogen ions. The cross-section of reaction (10), which involves argon ions in the excited state $^2P_{1/2}$, exceeds the cross-section of the same reaction for argon ions in the ground state $^2P_{3/2}$. These results are consistent with the theoretical estimates of the rate constants for the ion–molecule reaction (10).[28]

It has also been shown[26] that the formation of ArH^+ ions begins below the ionisation potentials of the hydrogen molecule and the argon atom for photon energies exceeding the predissociation threshold of the hydrogen molecule in the $D^1\Pi_u$ state (14.66 eV) and therefore may be attributed to the reaction of metastable hydrogen atoms with argon atoms:

$$H(2S) + Ar \rightarrow ArH^+ + e . \quad (11)$$

Argon atoms in the excited electronic state $4d[\frac{1}{2}]_1^0$ (14.71 eV) can also contribute to the formation of ArH^+ and Ar_2^+ ions in collisions with hydrogen molecules and other argon atoms:

$$Ar[4d[^1/_2]_1^0] + H_2 \rightarrow ArH^+ + (H + e) , \quad (12)$$

$$Ar[4d[^1/_2]_1^0] + Ar \rightarrow Ar_2^+ + e . \quad (13)$$

The lower limit of the proton affinity of argon determined on the hypothesis that reaction (11) involves thermal hydrogen atoms in the 2S state is 3.397 eV.

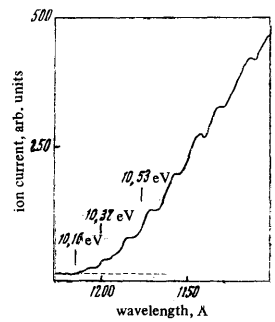


Figure 3. Photoionisation curve for ammonia.

3. Ammonia and Water

The photoionisation of ammonia molecules is characterised by a structure of the vibrational and autoionisation levels on the appearance curve for molecular ions at the first ionisation potential, which is 10.16 eV and corresponds to the removal of an electron from the ^2P_z orbital of the lone electron pair of nitrogen[29-31]. Fig. 3 shows that the initial section of the ammonia photoionisation curve consists of a series of steps, which is evidence of direct ionisation of the molecules in this range of photon

energies. At photon energies of 10.32 and 10.53 eV, the deformation and stretching vibrations of the radical-cations NH_3^+ are excited[30]. A contribution by autoionisation states appears with increase of photon energy.

The formation of excited electronic states of the ammonia radical-cations is observed at higher photon energies (15.31 eV) and involves the removal of an electron from the σ_{NH} orbital[32].

Ion–molecule reactions in ammonia have been investigated by the electron impact method[10,33,34]. Thus, using the method of the pulse withdrawal of ions, it has been shown[10] that the formation of NH_4^+ ions involves radical-cations at thermal velocities, starting with the ammonia ionisation threshold:

$$NH_3^{+\cdot} + NH_3 \rightarrow NH_4^+ + NH_2^{\cdot}. \qquad (14)$$

It has also been shown by the photoionisation method that the appearance potentials of NH_4^+ and $NH_3^{+\cdot}$ ions agree very closely (to within 0.01 eV)[30,31]. These findings suggest that reaction (14) involves the radical-cations $NH_3^{+\cdot}$ in the ground and excited vibrational states.

With increase of photon energy from the primary ionisation potential of ammonia (10.16 eV) upwards by 1.4 eV, the cross-section of the ion–molecule reaction (14) decreases approximately by 20%. This suggests that the yield of NH_4^+ ions in reaction (14) decreases with increasing vibrational excitation of the primary ammonia radical-cations when the vibrational quantum number increases from zero to nine.

Table 1. Heats of formation of molecules, radicals, and ions employed in the thermochemical calculations.

Species	$\Delta H_f^{298°K}$, eV	References	Species	$\Delta H_f^{298°K}$, eV	References
H	+2.26	37	CH_3OH	−2.08	41
NH_2	+1.73±0.08	38	C_2H_5OH	−2.44	41
NH_3	+0.48	39	CH_2O	−1.21	39
NH_4^+	+6.42	36	$CH_3CH{=}O$	−1.72	41
$OH^{\cdot}$	+0.40±0.04	38	$(CH_3)_2CO$	−2.24	39
H_2O	−2.51	39	$CH_3C{=}O^+$	+6.80±0.1	2
H_3O^+	+6.20±0.05	36	CH_3COCH_2	−0.52	38
CH_3O	+0.08±0.09	38	$(CH_3)_2CHOH$	−2.84	41
CH_3OH	−0.35±0.13	38	$(CH_3)_3COH$	−3.24	41
C_2H_5O	−0.30±0.09	38	C_6H_5	+3.12	38
CH_3CHOH^+	−0.80±0.13	38	$C_6H_5CH_2$	+1.92	38
$CH_2{=}OH^+$	+7.25±0.05	40	C_6H_6	+0.86	39
$CH_3CH{=}OH^+$	+6.10±0.05	40	$C_6H_5CH_3$	+0.52	39
$(CH_3)_2COH^+$	+5.10±0.05	40	$1,3\text{-}C_6H_4(CH_3)_2$	+0.18	39
$CH_3OH_2^+$	+6.00±0.13	11	cyclohexa-1,3-diene	+1.11	39
$C_2H_5OH_2^+$	+5.05±0.4	11	CH_3	+1.47	38

It has also been shown[31] that the change in the kinetic energy of the primary radical-cations $NH_3^{+\cdot}$, achieved by altering the gradient of the electric field withdrawing ions from the ionisation chamber of the mass-spectrometer, does not affect significantly the variation of the cross-section of reaction (14) with the internal energy of the primary radical-cations. This enabled the authors[31] to conclude that reaction (14) involves the formation of an intermediate "complex" in accordance with the statistical theory of ion–molecule reactions[35]. According to this theory, at the ammonia ionisation threshold reaction (14) proceeds via only one pathway with formation of NH_4^+ ions. With increase of the internal energy of the primary radical-cations $NH_3^{+\cdot}$, the probability of the reverse reaction increases, which leads ultimately to a decrease of the yield of NH_4^+ cations as the photon energy rises.

In contrast to reaction (14), the cross-section for the formation of NH_4^+ ions in the reaction between ammonia radical-cations and water molecules, which involves the transfer of a hydrogen atom, is independent of photon energy in the range from the ionisation potential upwards:

$$NH_3^{+\cdot} + H_2O \rightarrow NH_4^+ + HO^{\cdot}. \qquad (15.1)$$

Another pathway in this reaction involves the formation of H_3O^+ cations by transfer of a proton from the ammonia radical-cation to a water molecule:

$$NH_3^{+\cdot} + H_2O \rightarrow NH_2^{\cdot} + H_3O^+. \qquad (15.2)$$

Thermochemical calculations[36] based on the heats of formation of the cations NH_4^+ and H_3O^+ (Table 1) show that the heats of the exothermic ion-molecule reactions (14), (15.1), and (15.2) are 2.0, 1.3, and 0.2 eV respectively. The proton affinities of ammonia (9.0 eV) and water (7.16 eV) were also determined from the heats of formation of the cations NH_4^+ and H_3O^+.

III. ION–MOLECULE REACTIONS IN SATURATED AND UNSATURATED HYDROCARBONS

1. Olefins

The photoionisation of olefins in the region of the first ionisation potential involves the formation of radical-cations in the ground and excited states as the result of the removal of an electron from an upper π-type molecular orbital, which has a maximum electron density at the C–C bond. The interaction of π electrons with the electrons of the σ orbitals is fairly strong[42].

In the photoionisation of ethylene, deformation and stretching vibrations of the C–C bond at frequencies of 440 and 1400 cm^{-1} respectively are excited in the radical-cations at the ionisation threshold[43]. With increase of photon energy by 1–2 eV, the C–H bond vibrations and combination vibrations at a higher frequency are excited.

The radical-cations thus obtained exhibit a high reactivity in ion–molecule reactions in the photolysis and radiolysis of olefins and unsaturated hydrocarbons.

In the study of ion–molecule reactions in olefins, the mass-spectrometric photoionisation method was first employed by Koyano and coworkers[44,45]. It enabled them to determine various pathways in the formation of secondary products comprising ions of different structures, radicals, and molecules in the reaction between the radical-cations and molecules of the given olefin.

Ethylene[46]:

$$C_2H_4^{+\cdot} + C_2H_4 \rightarrow C_3H_5^+ + CH_3^{\cdot}, \qquad (16.1)$$

$$\rightarrow C_4H_7^+ + H^{\cdot}. \qquad (16.2)$$

Propene[44]:

$$C_3H_6^{+\cdot} + C_3H_6 \rightarrow C_3H_5^+ + C_3H_7^{\cdot} + H_2, \qquad (17.1)$$

$$\rightarrow C_3H_7^+ + C_3H_5^{\cdot}, \qquad (17.2)$$

$$\rightarrow C_4H_7^+ + C_2H_5^{\cdot}, \qquad (17.3)$$

$$\rightarrow C_4H_8^{+\cdot} + C_2H_4, \qquad (17.4)$$

$$\rightarrow C_5H_9^+ + CH_3^{\cdot}. \qquad (17.5)$$

But-1-ene[45]:

$$C_4H_8^{+\cdot} + C_4H_8 \rightarrow C_4H_7^+ + C_4H_9^\cdot , \quad (18.1)$$
$$\rightarrow C_4H_9^+ + C_4H_7^\cdot , \quad (18.2)$$
$$\rightarrow C_5H_9^+ + C_3H_7^\cdot , \quad (18.3)$$
$$\rightarrow C_5H_{10}^{+\cdot} + C_3H_6 , \quad (18.4)$$
$$\rightarrow C_5H_{11}^+ + C_3H_5^\cdot , \quad (18.5)$$
$$\rightarrow C_6H_{11}^+ + C_2H_5^\cdot , \quad (18.6)$$
$$\rightarrow C_6H_{12}^{+\cdot} + C_2H_4 . \quad (18.7)$$

But-2-ene[45]:

$$C_4H_8^+ + C_4H_8 \rightarrow C_4H_7^+ + C_4H_9^\cdot , \quad (19.1)$$
$$\rightarrow C_4H_9^+ + C_4H_7^\cdot , \quad (19.2)$$
$$\rightarrow C_5H_9^+ + C_3H_7^\cdot . \quad (19.3)$$

Isobutene[45]:

$$C_4H_8^{+\cdot} + C_4H_8 \rightarrow C_4H_7^+ + C_4H_9^\cdot , \quad (20.1)$$
$$\rightarrow C_4H_9^+ + C_4H_7^\cdot , \quad (20.2)$$
$$\rightarrow C_5H_9^+ + C_3H_7^\cdot . \quad (20.3)$$

Buta-1,3-diene[44]:

$$C_4H_6^{+\cdot} + C_4H_6 \rightarrow C_3H_3^+ + C_5H_9^\cdot , \quad (21.1)$$
$$\rightarrow C_4H_5^+ + C_4H_7^\cdot , \quad (21.2)$$
$$\rightarrow C_4H_7^+ + C_4H_5^\cdot , \quad (21.3)$$
$$\rightarrow C_5H_6^{+\cdot} + C_3H_6 , \quad (21.4)$$
$$\rightarrow C_5H_7^+ + C_3H_5^\cdot , \quad (21.5)$$
$$\rightarrow C_6H_7^+ + C_2H_5^\cdot , \quad (21.6)$$
$$\rightarrow C_6H_8^{+\cdot} + C_2H_4 , \quad (21.7)$$
$$\rightarrow C_7H_9^+ + CH_3^\cdot . \quad (21.8)$$

The ion–molecule reactions occurring in the photoionisation of olefins involving radical-cations can be divided into three main types.

1. Reactions (18.1), (19.1), (20.1), and (21.1), in which a hydrogen atom is transferred from the radical-cation to the olefin molecule (but-1-ene, but-2-ene, isobutene, and buta-1,3-diene) and which lead to the formation of the corresponding cations and alkyl radicals.

2. Reactions (17.2), (18.2), (19.2), (20.2), and (21.3), which lead to the formation of cations with a mass exceeding the molecular mass by unity and of radicals. It has been shown[47] that reactions of this type in propene and buta-1,3-diene involve the transfer of a hydrogen atom from the molecule to the radical-cation of the olefin.

3. Reactions involving a complex rearrangement of the atoms in the radical-cation and the molecule during collision. This applies in the first place to the formation of secondary ions and neutral species via the dissociation of C–H and C–C bonds in the initial species. Analysis of the velocity distribution of the ion–molecule reaction products in ethylene showed that reactions of this type proceed via a long-lived intermediate "complex", which ensures a redistribution of the energies of the colliding species among different degrees of freedom[45]. However, there are also exceptions for reactions of this type. For instance, the ion–molecule reaction in buta-1,3-diene leading to the formation of $C_3H_3^+$ ions and C_5H_9 radicals involves a direct mechanism.

2. Saturated and Unsaturated Hydrocarbons

Ion–molecule reactions play a significant role in the formation of secondary products in the radiolysis and photolysis of saturated and unsaturated hydrocarbons in the gas phase. The application of the mass-spectrometric photoionisation method permitted the determination of the principal pathways in these ion–molecule reactions and yielded information about the nature of their intermediate states.

Ion–molecule reactions of the first type include processes involving the transfer of H_2^- from the molecule to the radical-cation:

$$C_nH_m^{+\cdot} + AH_2 \rightarrow C_nH_{m+2} + A^{+\cdot} , \quad (22)$$

where AH_2 is a saturated hydrocarbon molecule and $C_nH_m^+$ the radical-cation of an unsaturated hydrocarbon or cyclopropane[48,49]. An example of this type of ion–molecule reactions occurring in the radiolysis of saturated hydrocarbons is the reaction between the propene radical-cations, formed in the decomposition of cyclopentane radical-cations, and cyclopentane molecules[50]:

$$C_3D_6^{+\cdot} + \text{cyclo-}C_5D_{10} \rightarrow C_3D_6 + C_5D_8^{+\cdot} . \quad (22.1)$$

The most systematic data on the mechanism of the ion–molecule reactions occurring in the photolysis of propene and unsaturated hydrocarbons and involving an H_2^- transfer have been obtained by Gorden and Ausloos[51]:

$$C_3D_6^{+\cdot} + AH_2 \rightarrow CD_3CDHCD_2H + A^{+\cdot} , \quad (22.2)$$

where AH_2 is a saturated hydrocarbon molecule (cycloalkanes, straight-chain and branched-chain alkanes). The contribution of other ion–molecule reactions to the formation of secondary products was excluded, since the experiments were performed at a photon energy of 10.0 eV, which is less than the ionisation potentials of the saturated hydrocarbons AH_2.

It is seen that the ion–molecule reaction in the photoionisation of propene and isobutane proceeds via an intermediate state the structure of which ensures the transfer of the HD^- species from the isobutane molecule to the propene radical-cation:

$$C_3D_6^{+\cdot} + (CH_3)_3CD \rightarrow C_3D_7H + C_4H_8^{+\cdot} . \quad (22.3)$$

It has been shown[51] that such an intermediate state ensures the transfer of a hydrogen atom from the CH_3 group of isobutane to the central atom of the $C_3D_6^{+\cdot}$ radical-cation and the formation of the propane molecule CD_3CDHCD_3. Such stereospecificity of the intermediate state in reactions of this type occurs also in the interaction between the propene radical-cation and the n-butane molecule:

$$C_3D_6^{+\cdot} + CD_3CH_2CH_2CD_3 \rightarrow C_3D_7H + CD_2CHCH_2CD_3^{+\cdot} . \quad (22.4)$$

The second important type of ion–molecule reactions in the photoionisation of the molecules in mixtures of saturated and unsaturated hydrocarbons includes H_2 transfer processes[50]:

$$C_nH_m + AH_2^{+\cdot} \rightarrow C_nH_{m+2} + A^{+\cdot} , \quad (23)$$

where C_nH_m is a cyclopropane or an unsaturated hydrocarbon molecule and $AH_2^{+\cdot}$ is the radical-cation of a saturated hydrocarbon. This type of reaction between the cyclohexane radical-cation and the cyclopropane molecule,

$$\text{cyclo-}C_6H_{12}^{+\cdot} + \text{cyclo-}C_3D_6 \rightarrow C_6H_{10}^{+\cdot} + C_3D_6H_2 , \quad (23.1)$$

involves the transfer of H_2 from the radical-cation and its addition to two carbon atoms with simultaneous ring opening and the formation of the propane molecule $CD_2HCD_2.CD_2H$.

It should be noted that in ion–molecule reactions of type (23), there is a competing process involving the

transfer of a hydrogen atom from the radical-cation to the molecule:

$$C_nH_m + AH_2^{+\cdot} \rightarrow C_nH_{m+1}^{\cdot} + AH^+. \quad (24)$$

Ion–molecule reactions at a high pressure (p = 20 torr) in a mixture of cyclobutane with saturated hydrocarbons, aliphatic amines, and other compounds have been investigated by the photoionisation method[52].

In a mixture of cyclobutane with alkanes and cycloalkanes, ion–molecule reactions proceeding via two pathways were observed: via the transfer of H^- and H_2^- from the AH_2 molecule (alkane or cycloalkane) to the radical-cation $C_4H_8^{+\cdot}$ formed in the photoionisation of cyclobutane ($h\nu \simeq 10.3$ eV):

$$C_4H_8^{+\cdot} + AH_2 \rightarrow C_4H_9^{+} + AH^+, \quad (25.1)$$

$$C_4H_8^{+\cdot} + AH_2 \rightarrow C_4H_{10} + A^{+\cdot}. \quad (25.2)$$

Ion–molecule reactions involving charge transfer in mixtures of cyclobutane with cyclohexane, trimethylamine, and nitric oxide were also observed in the same study.

IV. PHOTOIONISATION AND ION–MOLECULE REACTIONS IN KETONES AND ALCOHOLS

1. Alcohols

Systematic studies on the primary photoionisation and decomposition processes of aliphatic alcohols were first performed by Potapov and Sorokin[40] and Refaye and Chupka[53]. The application of the accurate photoionisation method made it possible to resolve the structure of the electronic and vibrational levels of the radical-cations on the photoionisation curves for alcohols recorded automatically on an MKh-1311 mass-spectrometer[1] and to determine the formation energies of fragment ions of different structures.

It was shown that ethanol radical-cations are formed mainly in excited electronic states at photon energies of 10.49 and 11.6 eV, which correspond to the removal of an electron from the $n(2P_y)$ orbital of the lone pair of oxygen and from the highest occupied σ orbital of the ground state respectively[40].

Data on the nature of the vibrational states of methanol and ethanol radical-cations excited in photoionisation have been obtained[40] by automatic differentiation of the initial sections of the photoionisation curves. The vibrational spectra of methanol (CD_3OH, CH_3OH, and CH_3OD) radical-cations shown in Fig. 4 are characterised by the presence of two principal bands. The first band (0–0 transition) corresponds to the first adiabatic ionisation potential of methanol, involving the removal of an electron from the lone pair of oxygen. The second band (900 cm^{-1}) may be assigned to the excitation of vibrations associated with the C–O bond. The relative intensity of these vibrations does not change when the hydrogen atom is substituted by a deuterium atom in the hydroxy-group but increases when the three hydrogen atoms in the methyl group are replaced by deuterium atoms. The probability of the formation of vibrationally excited radical-cations of ethanol is higher than the probability of their formation in the ground state. These findings indicate an increase of the C–O equilibrium bond length in the radical-cation on passing from CH_3OH to CD_3OH and C_2H_5OH.

Data on the mechanism of the decomposition of methanol and ethanol radical-cations on photoionisation were obtained[40] by analysing the simple mass spectra and appearance potentials of the fragment ions of the deuterated compounds CD_3OH and CH_3CD_2OH:

$$CD_3OH + h\nu \rightarrow CD_3OH^{+\cdot} + e, \quad (26.1)$$

$$CD_2OH^+ + D + e, \quad (26.2)$$

$$CH_3CD_2OH + h\nu \rightarrow CH_3CD_2OH^{+\cdot} + e, \quad (27.1)$$

$$CH_3CDOH^+ + D + e, \quad (27.2)$$

$$CD_2OH^+ + CH_3 + e. \quad (27.3)$$

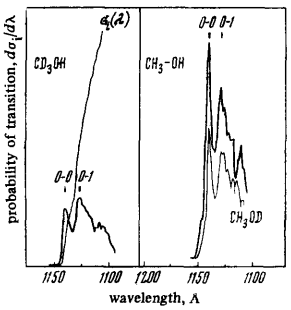


Figure 4. Vibrational spectra of radical cations.

Table 2. Appearance potentials of methanol and ethanol ions.

Compound	m/e	Type of ion	Appearance potential, eV
CD_3OH	35	$CD_3OH^{+\cdot}$	10.85±0.01
	34	$(CD_3O)^+$	12.0±0.05
	33	$CD_2{=}\overset{+}{O}H$	11.6±0.05
CH_3CD_2OH	48	$CH_3CD_2OH^{+\cdot}$	10.49±0.01
			11.6±0.1
	46	$CH_3CD{=}\overset{+}{O}H$	10.8±0.05
			11.7±0.1
	33	$CD_2{=}\overset{+}{O}H$	11.2±0.05
t-C_4H_9OH	59	$(CH_3)_2C{=}\overset{+}{O}H$	9.87±0.05
			11.0±0.1
			12.2±0.2

Table 2 shows that the decomposition processes which are energetically the most favourable are the decomposition reactions involving the dissociation of C–D and C–C bonds in the vibrationally excited radical-cations [reactions (26.2) and (27.2)] obtained by the removal of an electron from the lone pair of oxygen. These reactions involve a change in the initial electronic-nuclear configuration of the radical-cations with formation of the cations $CD_2{=}\overset{+}{O}H$ and $CH_3CD{=}\overset{+}{O}H$. The formation of $(CD_3O)^+$ ions from methanol is observed at a photon energy of 12.0 eV, which exceeds by 0.4 eV the appearance potential of the $CD_2{=}\overset{+}{O}H$ ions derived from CD_3OH [reaction (26.2)], but their yield is low. The $(CD_3O)^+$ ions formed via a rearrangement of the hydrogen and deuterium atoms have a structure of the type $CH_2{=}\overset{+}{O}H$, since the formation of CD_3O^+ ions by a direct removal of an electron from the σ orbital should occur at higher energies.

It is noteworthy that, according to the data of Brehm et al.[55], the dissociative photoionisation of methanol in the range of energies between the first and second ionisation potentials can also proceed via autoionisation states. However, in the case of ethanol the contribution by autoionisation states to the formation of fragment ions is already insignificant. The formation of $(CH_3CDOH)^+$ ions from CH_3CD_2OH at a photon energy of 11.7 eV, i.e. higher by 0.1 eV than the second ionisation potential, is associated with the decomposition of electronically excited radical-cations.

A characteristic feature of the photoionisation of t-butyl alochol[40] is the absence from the mass spectrum of an appreciable yield of molecular ions. The main dissociation process of t-butyl alcohol is the formation of $(CH_3)_2C{=}\overset{+}{O}H$ cations and methyl radicals in the range of energies from 9.87 eV upwards:

$$(CH_3)_3COH + h\nu \rightarrow (CH_3)_2C{=}\overset{+}{O}H + CH_3 + e \ . \qquad (28)$$

The yield of $(CH_3)_2C{=}\overset{+}{O}H$ cations increases appreciably at energies of 11.0 and 12.2 eV, corresponding to the second and third ionisation potentials of the t-butyl alcohol molecule.

Table 3. Ion–molecule reactions in methanol and ethanol[46].

Reactions		$-Q^{298°K}$*, eV	Reaction cross-section**
$CH_3OD^{+\cdot} + CH_3OD \rightarrow CH_3\overset{+}{O}D_2 + CH_3O$	(29.1)	0.6±0.1	1.0
$\rightarrow CH_3\overset{+}{O}DH + CH_2OD$	(29.2)	1.0±0.1	0.6
$CH_2\overset{+}{O}D + CH_3OD \rightarrow CH_3\overset{+}{O}D_2 + CH_2O$	(29.3)	0.4±0.1	2.7
$CH_3CD_2OH^{+\cdot} + CH_3CD_2OH \rightarrow CH_3CD_2\overset{+}{O}H_2 + CH_3CD_2O$	(30.1)	0.9±0.4	1.0
$CH_3CD_2OH^{+\cdot} + CH_3CD_2OH \rightarrow CH_3CD_2\overset{+}{O}HD + CH_3CDOH$	(30.2)	1.2±0.4	0.3
$\rightarrow CH_3CD_2\overset{+}{O}H_2 + CH_2CD_2OH$	(30.3)	1.2±0.4	0.06
$CD_2\overset{+}{O}H + CH_3CD_2OH \rightarrow CH_3CD_2\overset{+}{O}H_2 + CD_2O$	(30.5)	0.8±0.4	1.5
$CH_3C\overset{+}{D}OH + CH_3CD_2OH \rightarrow CH_3CD_2\overset{+}{O}H_2 + CH_3CDO$	(30.6)	0.2±0.4	

*Q is the heat of the ion–molecule reaction.
**The relative cross-sections for the reaction paths indicated in the Table correspond to a single dissociated bond.

The ion–molecule reactions occurring in the photon ionisation of methanol and ethanol[54] are exothermic, since the appearance potentials of the secondary cations agree to within 0.02 eV with the first ionisation potentials of methanol (10.85 eV) and ethanol (10.49 eV). This finding is consistent with data for ion–molecule reactions in alcohols obtained by the electron impact method using pulse withdrawal of ions[11].

Analysis of the changes in the mass spectra of methanol (CD_3OH, CH_3OD) and ethanol (CH_3CD_2OH, CD_3CH_2OH) as a function of the concentration of the alcohol in the ionisation chamber and of photon energy, carried out by Potapov and Sorokin[54], made it possible to determine the relative cross-sections for different pathways of ion–molecule reactions in both methanol and ethanol.

Table 3 shows that a general characteristic of ion–molecule reactions in alcohols involving primary radical-cations is that reactions (29.1) and (30.1), which yield secondary oxonium cations and the alkoxy-radicals CH_3O and CH_3CD_2O respectively, are more probable than reactions (29.2) and (30.2) involving the formation of secondary cations and methanol and ethanol radicals, despite the fact that the latter processes are energetically more favourable. In ethanol oxonium cations and the radicals CH_2CD_2OH are also formed but with a lower probability than that of the processes described above.

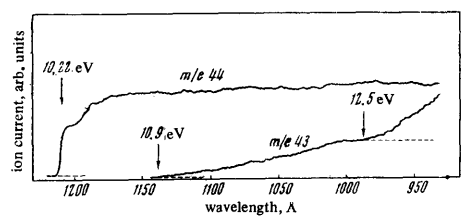


Figure 5. Appearance curves for molecular and fragment ions of acetaldehyde.

The different probabilities of ion–molecule reactions in alcohols by various pathways are determined by the interaction of the positive ion with the induced molecular dipole, which is a specific feature of polar molecules. In this case such an interaction between the radical-cation and the molecule leads to preliminary orientation of the molecule relative to the ion, which ensures the maximum probability of the ion–molecule reaction involving the transfer of a hydrogen atom (proton) from the O–H group. The probability of the reaction via this pathway relative to the reaction yielding secondary cations and radicals by the dissociation of the C_α–H bond is higher in ethanol than in methanol, probably owing to the greater polarisability of ethanol.

As already mentioned above, the electronic states of the methanol and ethanol radical-cations formed by the removal of an electron from the lone pairs of oxygen are characterised by the presence of a free valence localised at the oxygen atomic orbital. This explains the high reactivity of the alcohol radical-cations in their decomposition into cations of the type $CH_2{=}\overset{+}{O}H$ (methanol) and $CH_3CH{=}\overset{+}{O}H$ (ethanol). This feature should of course be observed also in ion–molecule reactions involving methanol and ethanol radical-cations. For this reason, one may postulate that the formation of heavier ions and radicals proceeds via the dissociation of the O–H (C–H) bond in the molecule and the addition of a hydrogen atom to the free valence of the radical-cation. This naturally does not rule out the possibility that ion–molecule reactions involving radical-cations can proceed via a proton transfer, for example from the OH group of the radical-cation to the molecule.

It has been shown[30,54] that near the first ionisation potentials the cross-sections of ion–molecule reactions in methanol and ethanol involving radical-cations are independent of the energy of the ionising photons and hence of the vibrational excitation of the radical-cations on photoionisation (Fig. 6). For reactions (29.2) and (30.2), which

lead to the formation of oxonium ions and methanol and ethanol radicals, the variation of the cross-section with photon energy persists also at photon energies exceeding the second ionisation potential of ethanol. This type of relation between the ionisation cross-sections for ion–molecule reactions and the internal energy of radical-cations is characteristic of processes involving the transfer of a hydrogen atom.

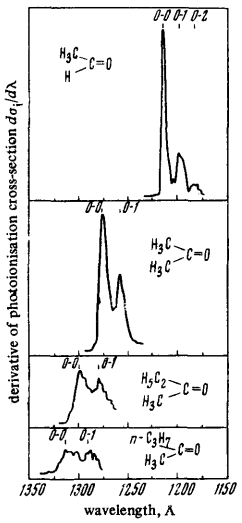


Figure 6. Vibrational spectra of the radical-cations of aliphatic ketones.

The cross-sections of ion–molecule reactions leading to the formation of oxonium ions $CH_3\overset{+}{O}D_2$ from CH_3OD and $CH_3CD_2\overset{+}{O}H_2$ from CH_3CD_2OH begin to increase at photon energies coresponding to the appearance potentials of the cations $CH_2{=}\overset{+}{O}D$ (CH_3OD) and $CH_3CD{=}\overset{+}{O}H$ (CH_3CD_2OH). This finding is evidence of the involvement of the cations $CH_2{=}\overset{+}{O}H$, $CH_3CD{=}\overset{+}{O}H$ and $CD_2{=}\overset{+}{O}H$ in the ion–molecule reactions (29.3), (30.4), and (30.5). This conclusion is consistent with the hypothesis of the involvement in ion–molecule reactions of fragment ions formed by electron impact[56]. Table 3 shows that these reactions are exothermic and proceed via the transfer of a proton from the hydroxy-group of the cation to the molecule with formation of the corresponding secondary oxonium ions and formaldehyde and acetaldehyde molecules.

2. Ketones

A characteristic feature of the electronic structure of aliphatic ketones is that the upper level of the ground state is occupied by the lone electron pair of oxygen[57]. This feature is clearly reflected in the presence of sharply rising sections in the photoionisation curves for acetaldehyde and acetone (see, for example, Fig. 5) near the first ionisation potentials, corresponding to the formation of radical-cations in the ground vibrational state by the removal of an electron from the $n(2P_y)$ orbital of the carbonyl oxygen[2]. The electronic states of the radical-cations formed in this way are characterised by the presence of a free valence localised at the atomic orbital of the heteroatom.

The vibrational spectra of the radical-cations of acetaldehyde, acetone, ethyl methyl ketone, and methyl n-propyl ketone, obtained by the automatic differentiation of the initial sections of the photoionisation curves and presented in Fig. 6, indicate the position of the 0–0 transition corresponding to the adiabatic ionisation potential and the 0–1 transition associated with the excitation of the vibrations of the C–O bond in the radical-cation[40]. The energies of these vibrations are in the range 0.14–0.15 eV for all the ketones mentioned above. This assignment of the vibrational bands of the radical-cations is consistent with data[58] showing that the vibrational energy of the C=O group in ketones, in excited electronic states, is of the order of 0.16 eV. The relative probability of the formation of the ketone radical-cations in the vibrational ground state, formed by the removal of an electron from the lone pair of oxygen, is a maximum, It decreases on passing from acetaldehyde to methyl n-propyl ketone, which is evidence that, with increase in the length of the aliphatic chain, the change in the equilibrium internuclear distance in the C=O bond of the radical-cations increases compared with the equilibrium internuclear distance in molecules in the ground state. It is of course reflected in a decrease of the relative intensity of the electronic 0–0 transition compared with the intensity of the 0–1 band corresponding to the C=O bond vibration. The mechanism of the interaction of the electrons of the radical-cation, leading to a change in bond length and order, depends on the change in the degree of overlap of the wave function of the unpaired electron of the lone pair of oxygen with the wave functions of the σ and π orbitals on passing from acetaldehyde to methyl n-propyl ketone.

The decrease in the adiabatic ionisation potentials of the ketones of the above series is correlated with the decrease of the C=O bond order of the molecule in the ground state and it has been shown[59] to be related to the increased polarity of this bond (increased negative charge at the oxygen atom).

At higher vibrational excitation energies, i.e. at ionising photon energies of 10.89 eV (acetaldehyde) and 10.42 eV (acetone), the interaction of the unpaired oxygen electron with the electrons of the σ orbitals leads to a change of the electronic-nuclear configuration of the radical-cation as a whole and its decomposition into the ion $CH_3{-}C{\equiv}O^+$ and the radical R:

$$\begin{matrix} R \\ H_3C \end{matrix}\!\!>\!C{=}O + h\nu \rightarrow \begin{matrix} R \\ H_3C \end{matrix}\!\!>\!C{=}O^{+\cdot} + e\ , \qquad (31.1)$$

$$\rightarrow CH_3{-}C{\equiv}O^{+} + R + e\ , \qquad (31.2)$$

where R = H or CH_3.

In the region of photon energies of 11.7 eV, the appearance curve for fragment ions of acetone shows an appreciable increase of the yield of the ions. The increased yield for this energy may be attributed to the decomposition of electronically excited acetone radical-cations:

$$(CH_3)_2CO + h\nu \rightarrow CH_3{-}\overset{+}{C}{=}O + CH_3 + e\ . \qquad (32)$$

The cations formed in this way have a structure different from that of $CH_3{-}C{\equiv}\overset{+}{O}$ formed in the decomposition of vibrationally excited radical-cations by reaction (31.2). For acetaldehyde, the formation of fragment ions with a mass of 43 by this pathway takes place at a higher energy (12.5 eV), corresponding to the second ionisation potential.

It has been shown[30] that at higher vapour pressures of acetaldehyde and acetone the mass spectra of these compounds reveal secondary cations, the origin of which may be accounted for as follows. In the collisions between radical-cations and molecules, the unpaired electron of the heteroatom enters into an exchange interaction with the electrons of the C–H bond of the molecule, which may become very intense (in the presence of the necessary overlapping of the electron clouds of the colliding species) and may lead to the dissociation of the C–H bond and the formation of a new bond in the ion:

$$CH_3CH=\overset{+\cdot}{O} + CH_3CH=O \rightarrow CH_3CH=\overset{+}{O}-H + CH_3CO\,, \qquad (33)$$

$$(CH_3)_2C=\overset{+\cdot}{O} + (CH_3)_2C=O \rightarrow (CH_3)_2C=\overset{+}{O}-H + CH_3COCH_2\,. \qquad (34)$$

The heats of the exothermic ion–molecule reactions (33) and (34) involving the transfer of a hydrogen atom, determined from the heats of formation of the reactant species, are −0.87 and −0.75 eV. The cross-section of reactions (33) and (34) in the range of photon energies between the first ionisation potential of acetaldehyde (10.22 eV) and acetone (9.71 eV) and above are independent of the photon energies. The increase of the yield of secondary cations, observed, for example, for acetone at an energy of 11.7 eV, is probably associated with the participation of cations formed in the decomposition of the molecule via mechanism (32):

$$CH_3-\overset{+}{C}=O + (CH_3)_2CO \rightarrow [(CH_3)_2COH]^+ + CH_3CO\,. \qquad (35)$$

Reaction (35) involves the dissociation of two bonds and the formation of two new bonds, the bond dissociation and formation processes occurring simultaneously in a single step during the collision period, i.e. via an intermediate "complex". Cations of the type $R-C\equiv\overset{+}{O}$ do not contribute to the formation of secondary cations, since thermochemical calculation shows that ion–molecule reactions with their participation are endothermic.

The knowledge of the heats of formation of the ions $CH_2=\overset{+}{O}H$, $CH_3CH=\overset{+}{O}H$, and $(CH_3)_2C=\overset{+}{O}H$, obtained by the photoionisation method[40], permits the determination of the proton affinities of formaldehyde (7.4 ± 0.05 eV), acetaldehyde (8.05 ± 0.05 eV), and acetone (8.5 ± 0.1 eV).

Studies on the photoionisation processes of acetone at a pressure of 10^{-3}–10^{-2} mmHg[68] led to the observation of ion–molecule reactions leading to the formation of a high yield of the associated ions M_2^+ and $(M+1).M_n^+$, where $n = 1, 2,$ or 3.

3. Ketones and Alcohols

Ion–molecule reactions in the photoionisation of the molecules in mixtures of ketones and alcohols have been investigated[60]. To identify different pathways of such reactions, deuterated specimens of acetone and ethanol were employed.

Analysis of the mass spectra of the molecules in the binary systems $(CH_3)_2CO-C_2H_5OD$ and $(CD_3)_2CO-C_2H_5OH$ showed that reactions involving acetone and ethanol radical-cations have the following mechanisms:

$$(CH_3)_2CO^{+\cdot} + C_2H_5OD \rightarrow (CH_3)_2C\overset{+}{O}D + C_2H_5O\,, \qquad (36)$$

$$(CD_3)_2CO + C_2H_5OH^{+\cdot} \rightarrow CD_3COCD_2 + C_2H_5OHD^+\,. \qquad (37.1)$$

The formation of the stable ions $(CH_3)_2C\overset{+}{O}D$ and $C_2H_5\overset{+}{O}HD$ involves the transfer of a deuterium atom from the molecules to the radical-cations $(CH_3)_2CO^{+\cdot}$ and $C_2H_5OH^{+\cdot}$ in the range of photon energies between the ionisation potentials of acetone (9.71 eV) and ethanol (10.49 eV) and above. Thermochemical calculation shows that the heats of these exothermic reactions [reactions (1) and (2)] are respectively −0.25 and −1.3 eV.

It has also been shown[60] that at photon energies from the ionisation potential of C_2H_5OD (10.48 eV) upwards, rapid formation of $(CH_3)_2C=\overset{+}{O}D$ ions is observed, which suggests that they are produced in reactions of molecular and fragment ions of C_2H_5OD with the molecules of acetone $(CH_3)_2CO$:

$$(CH_3)_2CO + C_2H_5OD^{+\cdot} \rightarrow (CH_3)_2C=\overset{+}{O}D + C_2H_5O\,, \qquad (37.2)$$

$$(CH_3)_2CO + CH_3CH=\overset{+}{O}D \rightarrow (CH_3)_2C=\overset{+}{O}D + CH_3CHO\,, \qquad (38)$$

$$(CH_3)_2CO + CH_2=\overset{+}{O}D \rightarrow (CH_3)_2C=\overset{+}{O}D + CH_2O\,. \qquad (39)$$

Reactions (37.2), (38), and (39) are exothermic (the heats are −1.0, −0.48, and −1.13 eV) and involve the transfer of a deuteron from ethanol ions to acetone. In this case the deuteron adds to the lone pair of oxygen. The neutral products of this reaction are the ethoxy-radical, acetaldehyde, and formaldehyde respectively. It is noteworthy that the fragment ions of ethanol make the principal contribution to the yield of the proton-transfer reactions between acetone and ethanol.

The reactions between the ions and the molecules of acetophenone and ethanol also proceed via two pathways. The reaction of the acetophenone radical-cations with ethanol molecules is accompanied by the transfer of a deuterium atom from C_2H_5OD and its addition at the oxygen free valence in the acetophenone radical-cation:

$$\begin{matrix} H_5C_6 \\ H_3C \end{matrix}\!\!>\!C=O^{+\cdot} + C_2H_5OD \rightarrow \begin{matrix} C_6H_5 \\ H_3C \end{matrix}\!\!>\!C=\overset{+}{O}D + C_2H_5O\,. \qquad (40)$$

The increase of the yield of the secondary acetophenone ions $C_6H_5C\overset{+}{O}DCH_3$ in the range of photon energies from 10.8 eV upwards is probably associated with reactions involving the transfer of a deuteron from ethanol fragment ions to the acetophenone molecule:

$$\begin{matrix} H_5C_6 \\ H_3C \end{matrix}\!\!>\!C=O + CH_3CH=\overset{+}{O}D \rightarrow \begin{matrix} H_5C_6 \\ H_3C \end{matrix}\!\!>\!C=\overset{+}{O}D + CH_3CHO\,, \qquad (41)$$

$$\begin{matrix} H_5C_6 \\ H_3C \end{matrix}\!\!>\!C=O + CH_2=\overset{+}{O}D \rightarrow \begin{matrix} H_5C_6 \\ H_3C \end{matrix}\!\!>\!C=\overset{+}{O}D + CH_2O\,. \qquad (42)$$

The ion–molecule reactions in ketones and alcohols involve the radical-cations formed by the removal of an electron from the upper orbital of the lone pair of the heteroatom and fragment ions. The reactions of the radical-cations with molecules involve the transfer of a hydrogen atom from the molecule to the radical-cation. The hydrogen atom adds to the heteroatom, which has a free valence, without a significant change in the structure of the radical-cations, i.e. without a complete redistribution of the energies of the colliding species among the degrees of freedom during the period of their interaction. This conclusion is confirmed by the independence of the cross-sections for these ion–molecule reactions of the excitation energy of the initial radical-cations. The reactions of the alcohol fragment ions with the molecules of alcohols and ketones take place via the transfer of a proton from the OH group of the fragment ion to the molecule. Here it is noteworthy that processes of this type make the principal contribution to the formation of the secondary ion–molecule reaction products in alcohols and ketones.

V. ION–MOLECULE REACTIONS IN AROMATIC HYDROCARBONS

Studies on ion–molecule reactions in aromatic hydrocarbons by the electron impact method have shown[61–63] that the formation of secondary products involves only fragment ions produced by the ionisation of the molecules (benzene, toluene). In these studies the failure to observe ion–molecule reactions between radical-cations and molecules which are not prohibited on energy grounds shows the passivity of the electronic states of the radical-cations of aromatic hydrocarbons produced by the removal of an electron from the π orbital of the ground state.

The problem of the mechanism of the ion–molecule reactions occurring in the photoionisation of "aromatic hydrocarbon–alcohol" mixtures was examined by Potapov and Sorokin[64]. To identify the reactions between ions and molecules of the "benzene–ethanol" system, two mixtures, $C_6D_6-C_2H_5OH$ and $C_6H_6-C_2H_5OD$, were chosen. By analysing the variation of the mass spectrum of the molecules of the mixtures with photon energy and concentration of the components, it was shown that the ion–molecule reactions in benzene and ethanol proceed via two paths (Fig. 7*a*):

$$C_6D_6 + C_2H_5OH^{+\cdot} \rightarrow C_6D_5 + C_2H_5OHD^+ , \quad (43)$$

$$C_6H_6 + CH_2{=}\overset{+}{O}D\,(C_2H_5OD) \rightarrow C_6H_6D^+ + CH_2O . \quad (44)$$

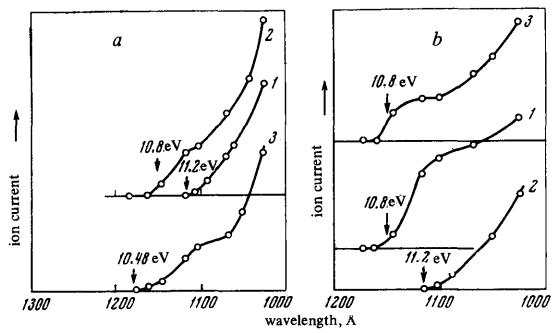


Figure 7. *a*) Appearance curves for the secondary ions of $C_6H_6D^+$ (curve *1*), toluene $C_7H_8D^+$ (curve *2*), and *m*-xylene $C_8H_{10}D^+$ (curve *3*); *b*) appearance curves for the primary ions of deuteroethanol CH_2OD^+ (curve *2*) and CH_3CHOD^+ (curve *1*) and secondary ions of naphthalene $C_{10}H_9D^+$ (curve *3*).

The heat of the exothermic reaction (43), involving the transfer of a deuterium atom from benzene to the radical-cation with formation of phenyl radicals, is 0.73 eV. Reaction (44), in which the benzene cations $C_6H_6D^+$ are formed, involves the transfer of a deuteron from the hydroxy-group of the $CH_2{=}\overset{+}{O}D$ cation. This is indicated by the identity of the appearance potentials of the $C_6H_6D^+$ and $CH_2{=}\overset{+}{O}D$ cations. This conclusion is consistent with data for the formation of $C_6H_7^+$ ions in benzene and ethanol, which was observed by the electron impact method at higher energies[65].

The appearance potentials of the secondary and primary ions show that three ion–molecule reactions take place between toluene and ethanol ($C_6D_5CD_3-C_2H_5OH$ and $C_6H_5CH_3-C_2H_5OD$ mixtures)[64]:

$$C_6D_5CD_3 + C_2H_5OH^{+\cdot} \rightarrow C_6H_5CD_2 + C_2H_5OHD^+ , \quad (45)$$

$$C_6H_5CH_3 + CH_3CHOD^+\,(C_2H_5OD) \rightarrow C_7H_8D^+ + CH_3CHO , \quad (46.1)$$

$$C_6H_5CH_3 + CH_2OD^+\,(C_2H_5OD) \rightarrow C_7H_8D^+ + CH_2O . \quad (46.2)$$

In contrast to the reactions in benzene and ethanol, in the "toluene–ethanol" system the secondary cations $C_7H_8D^+$ are formed by the transfer of a deuteron from the cation CH_3CHOD^+, which is evidence of a similarity of the appearance potentials of the cations $C_7H_8D^+$ and CH_3CHOD^+. A comparative estimate of the heats of ion–molecule reactions in toluene and ethanol showed that the cations $C_7H_8D^+$ can also be formed as a result of the transfer of a deuteron from the radical-cation $C_2H_5OD^{+\cdot}$. However, the yield of this reaction is probably much lower than those of reactions (46) and (47).

Ion–molecule reactions in *m*-xylene and ethanol, involving the transfer of protons from the ethanol radical-cation and fragment ions of the above type, have also been observed[64].

In view of the occurrence of the exothermic reactions (44) and (46), it is possible to determine the lower limits of the proton affinities of benzene and toluene: 7.44 and 8.05 eV. The proton affinity obtained for benzene agrees well with the value 7.46 eV determined[64] by the photoionisation method from the appearance potential of $C_6H_7^+$ ions derived from cyclohexa-1,3-diene.

The ion–molecule reactions occurring in the photoionisation of the molecules of "naphthalene–ethanol" and "anthracene–t-butyl alcohol" mixtures have been investigated[66] and it was shown that the secondary cations of naphthalene $C_{10}H_8D^+$ (see Fig. 7*b*) and anthracene $C_{14}H_{11}^+$ are formed in the reactions by the transfer of deuterons (protons) from the alcohol cations to the molecules of the aromatic hydrocarbons:

$$C_{10}H_8 + CH_3CHOD^+\,(C_2H_5OD) \rightarrow C_{10}H_8D^+ + CH_3CHO , \quad (47.1)$$

$$C_{10}H_8 + CH_2OD^+\,(C_2H_5OD) \rightarrow C_{10}H_8D^+ + CH_2O , \quad (47.2)$$

$$C_{14}H_{10} + (CH_3)_2COH^+\,((CH_3)_3COH) \rightarrow C_{14}H_{11}^+ + (CH_3)_2CO . \quad (48)$$

The lower limits of the proton affinities of naphthalene and anthracene determined from reactions (47.1) and (48) are respectively 8.05 and 8.5 eV.

Ion–molecule reactions involving the radical-cations of aromatic hydrocarbons A and leading to the formation of the cations AH^+ have not been observed[64,66]. Thermochemical calculation shows that in benzene and toluene reactions of this type are endothermic. However, as already mentioned above, despite the absence of an energy prohibition, bimolecular ion–molecule reactions involving benzene and toluene radical-cations also do not occur[61,62].

The low reactivity of the radical-cations of aromatic hydrocarbons may be due to the nature of the electronic states of the radical-cations generated on photoionisation by the removal of an electron from the occupied molecular π orbitals.

Trimolecular ion–molecule reactions involving the molecular ions of benzene and leading to the formation of the ions $C_{12}H_{12}^+$ have been observed[69]. The excess excitation energy of the "complex" is removed in this case by a third body.

VI. PROTON AFFINITY OF MOLECULES

Data on photoionisation and ion–molecule reactions yielded information about the structural characteristics of

the molecules A which determine their capacity to form stable cations AH^+ by combining with a proton. The stability of the cations is determined by the proton affinities of the compounds, which are listed in Table 4.

The formation of the cations AH^+ by aliphatic compounds containing the $\rangle C{=}O$ and O–H groups takes place as the result of the addition of a proton to the lone pair of electrons of the heteroatom. The stability of the alcohol cation increases on passing from methanol to ethanol, i.e. on replacement of a hydrogen atom by a methyl group, which results in an increase of electron density at the oxygen atom. In this case the proton affinity increases from 7.8 eV (methanol) to 8.4 eV (ethanol). The same type of variation in the stability of the cations is observed in the series formaldehyde < acetaldehyde < acetone. The proton affinity of these molecules increases from 7.4 to 8.5 eV for the same reason.

Table 4. Proton affinities of atoms and molecules.

Compound	Proton affinity, eV	Method of determination	References
H	2.70	Photoionisation	3
H_2	3.40	Chemi-ionisation	3
He	1.83	IMR in photoionisation	26
Ne	2.83	IMR in photoionisation	26
Ar	3.40	Chemi-ionisation	26
NH_3	9.0±0.05	Electron impact	36
H_2O	7.16±0.05	Electron impact	36
CH_3OH	7.8±0.13	IMR in electron impact	11
C_2H_5OH	8.4±0.4	IMR in electron impact	11
CH_2O	7.40±0.05	Photoionisation	60
CH_3CHO	8.05±0.05	Photoionisation	60
$(CH_3)_2CO$	8.5±0.05	Photoionisation	60
C_6H_6	7.46±0.03	Photoionisation	64
$C_6H_5CH_3$	8.05	IMR in photoionisation	64
Naphthalene	8.05	IMR in photoionisation	66
Anthracene	8.5	IMR in photoionisation	66

In aromatic hydrocarbons the stability of the cations formed in ion–molecule reactions increases with the number of rings, i.e. with decrease of the localisation energy, which is equal to the difference between the energies of the π-electron systems of the cation AH^+ and the molecule A. This feature is clearly reflected in the ion–molecule reactions involving aromatic hydrocarbons and alcohols and leading to the formation of the cations AH^+ as a result of proton transfer, and allows the conclusion that the addition of a proton to aromatic hydrocarbon molecules takes place by an electrophilic substitution mechanism. This implies that the proton adds to the carbon atom at which the π-electron density is a maximum and is accompanied by the formation of the cations AH^+ with the structure of a σ complex.

The high stability of the AH^+ cations of benzene, naphthalene, and anthracene formed in ion–molecule reactions (the affinity increases from 7.46 to 8.5 eV) is determined by the formation of a new σ_{CH} bond and a marked polarisation interaction, which becomes more intense with increasing number of π electrons in the aromatic hydrocarbons. The substitution of hydrogen atoms in benzene by an electron-donating group such as CH_3 also leads to an increase of the stability of the cations AH^+.

The data obtained on the stabilities of the cations are correlated with the basicity constants of the aromatic hydrocarbons[67].

REFERENCES

1. M. E. Akopyan, F. I. Vilesov, M. S. Komarov, V. A. Pavlenko, V. K. Potapov, and A. M. Shereshevskii, Khim. Vys. Energii, 3, 483 (1969).
2. V. K. Potapov, A. D. Filyugina, D. N. Shigorin, and G. A. Ozerova, Dokl. Akad. Nauk SSSR, 180, 398 (1968).
3. W. A. Chupka, M. E. Russell, and K. Refaye, J. Chem. Phys., 48, 1518 (1968).
4. Kh. S. Bagdasar'yan, Zhur. Vses. Khim. Obshch. im Mendeleeva, 11, 216 (1967).
5. V. L. Talrose and G. V. Karachevtsev, "Advances in Mass Spectrometry", The Elsevier Publishing Co., Amsterdam, 1966, Vol. 4, p. 211.
6. "Ion-molecule Reactions in the Gas Phase", Washington, Amer. Chem. Soc., 1966.
7. J. H. Futtrell and T. O. Tiernan, in "Fundamental Processes of Radiation Chemistry" (Edited by P. Ausloos), Interscience, New York, 1968.
8. V. L. Tal'roze and E. L. Frankevich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1351 (1959).
9. V. L. Tal'roze and E. L. Frankevich, Zhur. Fiz. Khim., 34, 2709 (1960) [Russ. J. Phys. Chem., No. 12 (1960)].
10. V. L. Tal'roze and E. L. Frankevich, Dokl. Akad. Nauk, SSSR, 111, 376 (1956).
11. E. L. Frankevich and V. L. Tal'roze, Zhur. Fiz. Khim., 33, 1093 (1959) [Russ. J. Phys. Chem., No. 5 (1959)].
12. E. L. Frankevich, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1957.
13. J. L. Franklin and M. A. Haney, J. Phys. Chem., 73, 2857 (1969).
14. L. V. Sumin and M. V. Gur'ev, Dokl. Akad. Nauk SSSR, 193, 858 (1970).
15. "Sixth International Conference on the Physics of Electronic and Atomic Collisions, Abstracts of Papers", Massachussetts, U. S. A., July 28–August 2, 1969.
16. E. E. Nikitin, Uspekhi Khim., 38, 1163 (1969) [Russ. Chem. Rev., No. 7 (1969)].
17. G. V. Karachevtsev, Khim. Vys. Energii, 4, 387 (1970).
18. F. J. Comes and U. Wenning, Z. Naturforsch., 24a, 1227 (1969).
19. V. V. Ivanov, V. A. Kaminskii, M. V. Tikhomirov, and N. N. Tunitskii, Khim. Vys. Energii, 3, 539 (1969).
20. S. E. Kupriyanov, Zhur. Eksper. Teor. Fiz., 48, 467 (1965).
21. V. W. Kaul, V. Lauterbach, and R. Taubert, Z. Naturforsch., 16a, 624 (1963).
22. M. W. Koch and L. Friedman, J. Chem. Phys., 38, 1115 (1963).
23. T. F. Moran and L. Friedman, J. Chem. Phys., 39, 2491 (1963).
24. F. S. Klein and L. Friedman, J. Chem. Phys., 41, 1789 (1964).
25. L. Friedman, Adv. Chem. Ser., 58, 87 (1966).
26. W. A. Chupka and M. E. Russell, J. Chem. Phys., 49, 5426 (1968).
27. W. A. Chupka, J. Berkowitz, and M. E. Russell, see Ref. 15, p. 71.
28. G. Gioumouss and D. P. Stevenson, J. Chem. Phys., 29, 294 (1958).
29. K. Watanabe and J. R. Mottl, J. Chem. Phys., 26, 1773 (1957).
30. V. K. Potapov, Dokl. Akad. Nauk SSSR, 183, 386 (1968).

31. W. A. Chupka and M. E. Russell, J. Chem. Phys., 48, 1527 (1968).
32. D. C. Frost and C. A. McDowell, Canad. J. Chem., 36, 39 (1958).
33. L. M. Dorman and P. C. Noble, J. Phys. Chem., 63, 908 (1959).
34. G. A. W. Derwich, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, J. Chem. Phys., 39, 1599 (1963).
35. J. C. Light, J. Chem. Phys., 40, 3231 (1964); J. C. Light and J. Lin, J. Chem. Phys., 43, 3209 (1965).
36. M. A. Haney and J. L. Franklin, J. Chem. Phys., 50, 2028 (1969).
37. V. I. Vedeneev, L. V. Gurvich, V. N. Kondrat'ev, M. A. Medvedev, and E. L. Frankevich, Handbook, "Energiya Razryva Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd. Akad. Nauk SSSR, Moscow, 1962.
38. J. A. Kerr, Chem. Rev., 66, 465 (1966).
39. M. Kh. Karapet'yants and M. L. Karapet'yants, "Osnovnye Termodinamicheskie Konstanty Neorganicheskikh i Organicheskikh Veshchestv" (Fundamental Thermodynamic Constants of Inorganic and Organic Substances), Izd. Khimiya, Moscow, 1968.
40. V. K. Potapov and V. V. Sorokin, Khim. Vys. Energii, 4, 365 (1970).
41. R. R. Bernecker and F. A. Long, J. Phys. Chem., 65, 1565 (1961).
42. M. J. S. Dewar and S. D. Worley, J. Chem. Phys., 50, 654 (1969).
43. R. Botter, V. H. Dibeler, J. A. Walker, and H. M. Rosenstock, J. Chem. Phys., 45, 1298 (1966).
44. I. Koyano, I. Omura, and I. Tanaka, J. Chem. Phys., 44, 3850 (1966).
45. I. Koyano, J. Chem. Phys., 45, 706 (1966).
46. M. Durup and J. Durup, "Advances in Mass Spectrometry" (Edited by E. Kendrick), London, 1968, Vol. 4, p. 677.
47. V. L. Tal'roze and A. K. Lyubimova, Dokl. Akad. Nauk SSSR, 86, 905 (1952).
48. G. Gerwich, A. Galli, A. Giardini-Guidoni, and G. Volpi, J. Chem. Phys., 41, 2998 (1964).
49. G. G. Meisels, Adv. Chem. Ser., 58, 243 (1966).
50. R. D. Doepker and P. Ausloos, J. Chem. Phys., 44, 1951 (1966).
51. R. Gorden, Jnr. and P. Ausloos, J. Chem. Phys., 47, 1709 (1967).
52. L. W. Sieek, S. K. Searks, and P. Ausloos, J. Amer. Chem. Soc., 91, 7627 (1969).
53. R. M. Refaye and W. A. Chupka, J. Chem. Phys., 48, 5205 (1968).
54. V. K. Potapov and V. V. Sorokin, Dokl. Akad. Nauk SSSR, 192, 590 (1970).
55. B. Brehm, V. Fuchs, and P. Kebarle, Int. J. Mass. Spectr. Ion Phys., 6, 279 (1971).
56. K. R. Rayn, L. L. Sieek, and J. H. Futtrell, J. Chem. Phys., 41, 111 (1964).
57. F. I. Vilesov, Uspekhi Fiz. Nauk, 31, 667 (1963).
58. R. M. Hexter, J. Opt. Soc. Amer., 53, 703 (1963).
59. A. D. Walsh, Trans Faraday Soc., 42, 56 (1946).
60. V. K. Potapov and V. V. Sorokin, Khim. Vys. Energii, 4, 556 (1970).
61. L. I. Virin, F. A. Safin, and R. V. Dzhagatspanyan, Khim. Vys. Energii, 1, 417 (1967).
62. L. I. Virin, F. A. Safin, R. V. Dzhagatspanyan, and G. V. Motsarev, Khim. Vys. Energii, 3, 23 (1969).
63. Ch. Lifshitz and B. G. Reuben, J. Chem. Phys., 50, 951 (1969).
64. V. K. Potapov and V. V. Sorokin, Khim. Vys. Energii, 4, 459 (1970).
65. H. D. Klotz, H. Drost, and W. Schulz, Z. Phys. Chem. (Leipzig), 237, 305 (1968).
66. V. K. Potapov and V. V. Sorokin, Dokl. Akad. Nauk SSSR, 195, 616 (1970).
67. "New Problems in Physical Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1969, p. 257.
68. M. E. Akopyan, Yu. L. Sergeev, and F. I. Vilesov, Uspekhi Fotoniki, 2, 75 (1971).
69. Yu. L. Sergeev, M. E. Akopyan, and F. I. Vilesov, Teor. Eksper. Khim., 7, 407 (1971).

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