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Abstract

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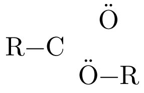
PHOTOIONIZATION OF ETHERS AND METAL CARBONYLS IN THE GASEOUS PHASE

(Presented by Academician A. N. Terenin, 30 V 1961)

In the work of one of the authors (1), the photoionization method was used to obtain values of the first adiabatic ionization potentials of a number of compounds whose molecules contain a carbonyl group. In the case of ketones it was shown that the induction interaction between the carbonyl and methyl groups obeys the law of additivity and decreases inversely proportional to the square of the distance between these groups. In order to verify the validity of these regularities for other classes of compounds, in the present work the photoionization method (2) was used to measure the first adiabatic ionization potentials of esters and some of their halogen derivatives, as well as of a series of simple ethers and several volatile metal carbonyls. As in the case of ketones, in these classes of compounds the first ionization potentials are determined by the removal of one of the valence electrons of oxygen that do not participate in the chemical bond. The obtained values of the ionization potentials are given in Tables 1, 2, and 3, where they are arranged by classes of compounds in order of decreasing ionization potentials.

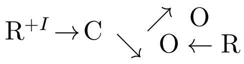
The first ionization potentials of esters are 0.45–0.55 eV higher than the ionization potentials of the corresponding ketones, which indicates a decrease in the electron density in the vicinity of the oxygen atom of the carbonyl group. The unshared electron pairs of the oxygen of the ether group are conjugated with the π-electrons of the carbonyl group. This causes a decrease in the positive charge in the vicinity of the carbon atom, which is expressed in a lowering of the reactivity of the carbonyl group toward nucleophilic reagents (3)



$$\mathrm{R{-}C}\begin{array}{l}\ddot{\mathrm{O}}\\ \ddot{\mathrm{O}}{-}\mathrm{R}\end{array}$$

This, apparently, should contribute to some increase in the electron density in the vicinity of the oxygen atom of the carbonyl group and to a decrease in the ionization potentials in esters as compared with the corresponding ketones.

The opposite result obtained experimentally indicates that in the present case transfer of electronic charge by the conjugation effect to the oxygen atom of the carbonyl group does not occur or occurs only insignificantly in comparison with the negative induction effect, which is due to the oxygen atom of the ether group. Consequently, changes in the ionization potentials in esters occur as the result of the superposition of the positive induction effect of the alkyl groups and the negative induction effect of the oxygen atom of the ether group



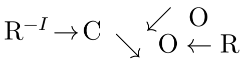


Table 1

Compound	Compound	Ionization potential, eV	Ionization potential of ketone, eV	Difference, eV
Ethyl acetate	$CH_3C(=O)OC_2H_5$	$10,08 \pm 0,02$	9,54	0,54
n-Propyl acetate	$CH_3C(=O)OC_3H_7$	$10,02 \pm 0,02$	9,47	0,55
n-Butyl acetate	$CH_3C(=O)OC_4H_9$	$10,00 \pm 0,03$	9,44	0,56
Iso-butyl acetate	$CH_3C(=O)OCH_2CH(CH_3)_2$	$9,94 \pm 0,03$	9,36	0,58
n-Pentyl acetate	$CH_3C(=O)OC_5H_{11}$	$9,92 \pm 0,02$	9,40	0,52
Methyl butyrate	$C_4H_9C(=O)OCH_3$	$9,87 \pm 0,02$	9,44	0,43
Ethyl valerate	$C_5H_{11}C(=O)OC_2H_5$	$9,67 \pm 0,03$	9,19	0,48
Butyl butyrate	$C_4H_9C(=O)OC_4H_9$	$9,57 \pm 0,03$	9,10	0,47

The last column of Table 1 gives the differences of the ionization potentials between the esters and the corresponding ketones. In the case of lengthening of the alkyl chain in the ether group, this difference, within the experimental error of $\pm 0,02 \div 0,03$ eV, remains constant and equal to $0,55$ eV, which undoubtedly indicates a high additivity of inductive effects directed in opposite directions. The differences between the ionization potentials of neighboring members of the given series of esters decrease as the length of the alkyl chain increases and, with high accuracy, as in the case of ketones, can be represented in the form of an inverse-square dependence on the distance from the hydrogen atom being replaced by a methyl group to the ether oxygen

$$\Delta I_p \simeq \frac{K}{[l(n+1)]^2},$$

where ΔI_p is the difference of the ionization potentials between two neighboring members of the series; $l(n+1)$ is the relative distance between the ether oxygen and the hydrogen atom that is replaced by a methyl group and forms the $(n+1)$ member of the series; k is a constant having, as in the case of ketones, a numerical value approximately equal to $0,7$ eV. The high additivity of inductive effects observed upon lengthening of the ether group is somewhat disturbed upon lengthening of the alkyl group directly attached to the carbonyl carbon. Thus the difference in the ionization potentials of the methyl ester of butyric acid and methyl butyl ketone is only $0,43$ eV. However, for the butyl ester of butyric acid it increases to $0,47$ eV. Such nonequivalence of the alkyl groups may be caused by weakening of the inductive effect by the chain of conjugated bonds O—C = O or by a spatial factor.

The regularities presented can be successfully used for estimating the first adiabatic ionization potentials of esters with an accuracy no worse than $0,05$—$0,1$ eV.

The additivity of various inductive effects, which change the ionization potential of esters with an accuracy up to $0,02$—$0,03$ eV, is preserved

Table 2

Compound	Ionization potential, eV	Ionization potential of the ether, eV	Ionization potential of the ketone, eV
Methyl ester of monochloroacetic acid`ClCH$_{2}$CH$_{3}$ —O>C=O`	10.35 ± 0.03	10.25	9.71
Methyl ester of dichloroacetic acid`Cl$_{2}$CHCH$_{3}$ —O>C=O`	10.44 ± 0.03	10.25	9.71
Ethyl ester of monochloroacetic acid`ClCH$_{2}$C$_{2}$H$_{5}$ —O>C=O`	10.20 ± 0.03	10.08	9.54
Ethyl ester of trichloroacetic acid`Cl$_{3}$CC$_{2}$H$_{5}$ —O>C=O`	10.44 ± 0.03	10.08	9.54

Compound	Ionization potential, eV	Ionization potential of the ether, eV	Ionization potential of the ketone, eV
Ethyl ester of monobromoacetic acidBrCH$_{2}$C$_{2}$H$_{5}$ —O>C=O	10.13 ± 0.03	10.08	9.54
Ethyl ester of monobromobutyric acidBrCH$_{2}$CH$_{2}$CH$_{2}$C$_{2}$H$_{5}$ —O>C=O	9.85 ± 0.02	—	9.26

for their halogen derivatives, where the negative inductive effect of the ether oxygen is enhanced by the halogen atom. To illustrate this, Table 2 gives the ionization potentials of some chloro- and bromo-derivatives of acetic-acid esters. For comparison, the ionization potentials of the unsubstituted esters and the corresponding ketones are also given. It is seen from Table 2 that replacement by chlorine of a hydrogen atom in the methyl group attached directly to the carbonyl carbon leads to an increase in the ionization potential by 0.10 ± 0.02 eV. Upon replacement of two

Table 3

Compound	Ionization potential, eV
Ethyl etherC$_{2}$H$_{5}$C$_{2}$H$_{5}$>O	9.55 ± 0.03
n-Propyl etherC$_{3}$H$_{7}$C$_{3}$H$_{7}$>O	9.28 ± 0.05
n-Butyl etherC$_{4}$H$_{9}$C$_{4}$H$_{9}$>O	9.18 ± 0.05
ChlorexClCH$_{2}$CH$_{2}$ClCH$_{2}$CH$_{2}$>O	9.85 ± 0.03
TetrahydrofuranCH$_{2}$—CH$_{2}$CH$_{2}$—CH$_{2}$>O	9.49 ± 0.02
Dimethyl sulfoxideCH$_{3}$CH$_{3}$>S=O	8.85 ± 0.05
Chromium carbonylCCr(CO)$_{6}$	8.03 ± 0.03
Molybdenum carbonylMo(CO)$_{6}$	8.12 ± 0.03
Tungsten carbonylW(CO)$_{6}$	8.18 ± 0.03
Iron carbonylFe(CO)$_{5}$	7.95 ± 0.03

Compound	Ionization potential, eV
Nickel carbonyl`Ni(CO)$_{4}$`	8.28 ± 0.03
Diethyl ketone`C$_{2}$H$_{5}$COC$_{2}$H$_{5}$`	9.34 ± 0.02
Ethyl *tert*-butyl ketone`C$_{2}$H$_{5}$CO(CH$_{3}$)$_{3}$C`	8.98 ± 0.02
Iso-propyl *tert*-butyl ketone`(CH$_{3}$)$_{2}$CHCOC(CH$_{3}$)$_{3}$`	8.82 ± 0.02

and three hydrogen atoms leads to an increase in the ionization potential by, respectively, 0.18 and 0.36 eV, which agrees well with the rule of additivity. Replacement of a hydrogen atom by bromine leads to an analogous but approximately two times smaller effect, which is easy to understand, since bromine has a lower electronegativity than chlorine.

Table 3 gives the values of the ionization potentials of a series of simple ethers, ketones, and some volatile metal carbonyls. The ionization energies of these compounds are unknown or have been measured with low accuracy (4).

In the case of simple ethers, no sharp breaks are observed in the photoionization curves, which may be caused by a significant difference between the interatomic distances in the molecule and in the corresponding positive ion; the ionization potentials are therefore determined with a large error (0.05 eV). Such large errors do not make it possible to establish reliably a quantitative dependence between molecular structure and ionization potentials, although qualitatively the character of the decrease in ionization potentials is analogous to that for complex ethers. It seems to us that this indicates that, upon ionization, one of the p-electrons of the oxygen atom is removed, which does not participate in the formation of the chemical bond. From the example of diethyl ether and tetrahydrofuran, whose ionization potentials are respectively 9.53 and 9.49 eV, it is evident that cyclization, as in the case of ketones, leads to a decrease in the ionization potential. The ionization potentials of some ketones given in Table 3 are in complete agreement with the quantitative relationships discussed earlier in work (1).

The first ionization potentials of metal carbonyls given in Table 3 are probably due to the removal of one of the valence electrons participating in the formation of the metal-carbon bond, or of one of the p-electrons of the oxygen atom of the carbonyl group. The small difference (0.2–0.3 eV) in the values of the ionization potentials of carbonyls of different metals (whereas the ionization potentials of metal atoms differ by 1.0–1.2 eV), and also the magnitudes of the ionization potentials, close to 8 eV, indicate that the metal-carbon bond is to a considerable degree double, while the carbonyl bond is to some degree triple. The slight increase in ionization potentials in the series of carbonyls of chromium, molybdenum, and tungsten is evidently associated with the increase in the ionization potentials of the atoms of the corresponding metals. These conclusions, following from the ionization potentials obtained, are in agreement with data on intramolecular bond lengths.

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Note: Figure translations are in progress. See original paper for figures.