# F. I. Vilesov

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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

**F. I. Vilesov**

# PHOTOIONIZATION OF VAPORS OF COMPOUNDS WHOSE MOLECULES CONTAIN A CARBONYL GROUP

*(Presented by Academician A. N. Terenin, January 25, 1960)*

The most accurate values of the ionization potentials of several simple aldehydes and ketones were obtained by the spectroscopic method by Price and Walsh ([1]). They also showed that the first ionization potentials of aliphatic compounds containing a carbonyl group are due to the removal of one of the unshared *p*-electrons of the oxygen of the carbonyl group. Since in these compounds the electron removed upon ionization belongs to the electrons localized at the oxygen atom, the magnitude of the ionization potential depends on the density of the electron cloud in the vicinity of the latter. This circumstance opens the possibility, by means of ionization potentials, of tracing the mutual influence of atoms and radicals entering into a complex molecule.

To determine the ionization potentials in the present work we used the procedure described earlier ([2]). The obtained values of the ionization potentials are collected in Tables 1 and 2.

**Table 1**

*First ionization potentials of aldehydes and ketones*

| Compound | Formula | Ionization potential, eV | Difference, eV | Compound | Formula | Ionization potential, eV |
|---|---|---|---|---|---|---|
| Formaldehyde | $H_2C{=}O$ | 10.90 ± 0.03 | 0.7 | Propyl butyl ketone | $C_3H_7COC_4H_9$ | 9.10 ± 0.05 |
| Acetaldehyde | $CH_3CHO$ | 10.20 ± 0.03 | 0.51 | Diisobutyl ketone | $C_4H_9COC_4H_9$ | 9.04 ± 0.03 |
| Dimethyl ketone | $CH_3COCH_3$ | 9.71 ± 0.03 | 0.17 | Cyclopentanone | $(CH_2)_4CO$ | 9.42 ± 0.03 |
| Methyl ethyl ketone | $CH_3COC_2H_5$ | 9.54 ± 0.03 | 0.07 | Cyclohexanone | $(CH_2)_5CO$ | 9.14 ± 0.03 |

| Compound | Formula | Ionization potential, eV | Difference, eV | Compound | Formula | Ionization potential, eV |
|---|---|---|---|---|---|---|
| Methyl propyl ketone | $CH_3COC_3H_7$ | $9.47 \pm 0.03$ | 0.03 | Pinacolin | $(CH_3)_3CCOCH_3$ | $9.18 \pm 0.03$ |
| Methyl butyl ketone | $CH_3COC_4H_9$ | $9.44 \pm 0.03$ | | Pivalone | $(CH_3)_3CCOC(CH_3)_3$ | $8.65 \pm 0.03$ |
| Methyl hexyl ketone | $CH_3COC_6H_{13}$ | $9.40 \pm 0.03$ | | Camphor | $C_{10}H_{16}O$ | $8.76 \pm 0.03$ |
| Dipropyl ketone | $C_3H_7COC_3H_7$ | $9.12 \pm 0.03$ | | | | |

In aliphatic compounds only such a type of interaction is possible as, in the classification of chemists, has been called the positive inductive effect $(+I)$. According to current concepts, the inductive interaction decreases in the series

$$C_4H_9 > C_3H_7 > C_2H_5 > CH_3 > H.$$

The ionization potentials given in Table 1 are in good agreement with this concept.

If one assumes that the change in ionization potentials in the given series is a linear function of the inductive effect, then, consider-

considering each subsequent member of the series as a methyl-substituted preceding one, it is easy to see that the inductive interaction decreases inversely proportional to the square of the distance between the methyl and carbonyl groups. Indeed, replacement of a hydrogen atom in formaldehyde by a $CH_3$ group leads to a decrease in the ionization potential by 0.7 eV.

**Table 2**

**Ionization potentials**

| Compound | Ionization potential, eV | Compound | Ionization potential, eV |
|---|---|---|---|
| $\genfrac{}{}{0pt}{}{H}{H}{>}C=O$ | $10.90 \pm 0.03$ | $\genfrac{}{}{0pt}{}{CH_3}{H}{>}C=O$ | $10.20 \pm 0.03$ |
| $\genfrac{}{}{0pt}{}{H}{CH_3}{>}C=O$ | $10.20 \pm 0.03$ | $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C=O$ | $9.71 \pm 0.03$ |
| $\genfrac{}{}{0pt}{}{H}{NH_2}{>}C=O$ | $10.16 \pm 0.03$ | $\genfrac{}{}{0pt}{}{CH_3}{NH_2}{>}C=O$ | $9.65 \pm 0.03$ |

| Compound | Ionization potential, eV | Compound | Ionization potential, eV |
|---|---|---|---|
| $\genfrac{}{}{0pt}{}{\text{H}}{\text{OH}}\!> \text{C} = \text{O}$ | $11.05 \pm 0.03$ | $\genfrac{}{}{0pt}{}{\text{CH}_3}{\text{OH}}\!> \text{C} = \text{O}$ | $10.38 \pm 0.03$ |

The second $CH_3$ group, directly attached to the carbonyl group, lowers the ionization potential by another 0.5 eV. If in dimethyl ketone one of the hydrogen atoms is replaced by a $CH_3$ group, then it will already be at a distance from the carbonyl group doubled in comparison with the same distance in acetaldehyde, and the decrease in the ionization potential should be 4 times smaller, as is observed experimentally.

The ionization potentials of higher members of the series also obey this regularity, and we may write the approximate relation

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

where $\Delta I_p$ is the difference in ionization potentials between two neighboring members of the series; $l(n+1)$ is the relative distance between the carbonyl group and the hydrogen atom that is replaced by the methyl group, the $(n+1)$th member of the series being formed.

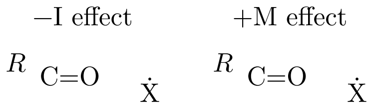
Such a dependence is valid not only for linear saturated ketones, but also for more complex branched ketones, the ionization potentials of which are given in Table 1. Examination of the values of the first ionization potentials of these compounds shows that the inverse proportionality of the difference of the ionization potentials to the square of the distance between the substituting methyl group and the carbonyl group obeys the rule of additivity with good accuracy. Indeed, pinacoline may be regarded as acetone in which 3 hydrogen atoms have been replaced by methyl groups. Replacement of a hydrogen atom by one methyl group in acetone leads to a decrease in the ionization potential by 0.17 eV. Hence, the ionization potential of pinacoline should be 0.51 eV less than the ionization potential of acetone, i.e., 9.20 eV; experimentally we have $9.18 \pm 0.03$ eV. An analogous consideration of pivalone, which may be regarded as acetone in which all 6 atoms have been replaced by methyl groups, leads us to an ionization potential of 8.69 eV; experimentally we have $8.65 \pm 0.03$ eV.

The regularities under discussion are apparently valid not only for ketones, where there is only a positive inductive effect, but also for their halogen derivatives, where there is a negative inductive effect (−I), which should lead to an increase in the ionization potential. As an illustration we give the ionization potentials of chloroacetone, $9.91 \pm 0.03$ eV, and dichloroacetone, $10.12 \pm 0.03$ eV, which were measured by us in the present work. The values of the ionization potentials of these compounds are, respectively, 0.20 and 0.41 eV higher than the ionization potential of acetone, equal to 9.71 eV.

The regularities found experimentally can be used not only to elucidate the mutual influences of functional groups in molecules, but also to estimate the ionization potentials of more complex saturated ketones.

Table 2 presents the ionization potentials of certain aldehydes, ketones, amides, and acids. In the last two cases, in addition to the inductive effect, a conjugation effect is present. Since the $NH_2$ and OH groups have a greater electron affinity than a hydrogen atom, the direction of the inductive effect will be opposite to the case of aliphatic radicals (−I). The conjugation effect, which in this case has a sign opposite to that of the inductive effect, is due to the mobility of the lone pairs of electrons of the substituent atoms, which are incorporated into the orbitals of the oxygen atom of the carbonyl group, increasing the electron density concentrated near it.

Both effects in amides and acids may be represented schematically as:



$$\overset{-\text{I effect}}{{}^{R}\,\mathrm{C{=}O}\quad \dot{\mathrm{X}}} \qquad\qquad \overset{+\text{M effect}}{{}^{R}\,\mathrm{C{=}O}\quad \dot{\mathrm{X}}}$$

X denotes the group $NH_2$ or OH. Since these effects cause displacement of electrons in opposite directions, the magnitude of the ionization potentials makes it possible to judge which effect predominates.

As is seen from Table 2, the ionization potentials of formamide and acetamide are, respectively, 0.74 and 0.55 eV lower than those of formaldehyde and acetaldehyde, and are even somewhat lower than the ionization potentials of acetaldehyde and dimethyl ketone (by 0.04 and 0.06 eV, respectively). This indicates the predominance of the positive conjugation effect, which enriches the electron density of the oxygen atom in the carbonyl group. Consideration of the ionization potentials of acids indicates that for them, on the contrary, the action of the negative inductive effect predominates, i.e., the electronic charge is displaced toward the hydroxyl oxygen atom. These conclusions agree with the fact that, according to chemical data ($^3$), the positive conjugation effect decreases in the series

$$N(CH_3)_2 > NH_2 > OH > Cl,$$

and the negative inductive effect decreases in the series

$$OH > NH_2 > NHCH_3 > N(CH_3)_2 > H.$$

We note that in work (4) the ionization potentials of these same compounds were measured by electron impact, and the data obtained differ substantially from ours. The authors, in analyzing their results, ascribe to amides a negative inductive effect exceeding the conjugation effect, which clearly does not agree with the lowering of the basicity of the $NH_2$ group in amides as compared with amines.

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Physical Institute
of Leningrad State University
named after A. A. Zhdanov

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