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ON THE QUESTION OF CONJUGATION IN BUTADIENE

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Abstract

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CHEMISTRY

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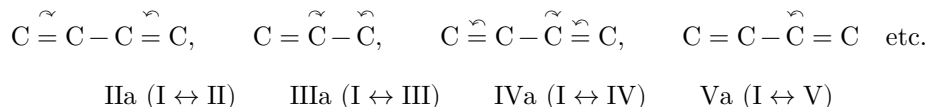
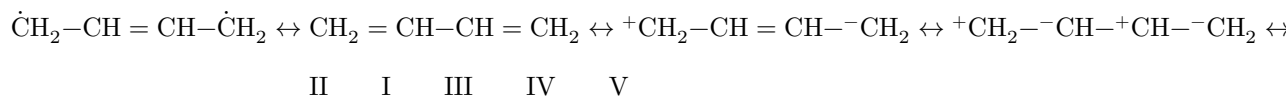
ON THE QUESTION OF CONJUGATION IN BUTADIENE

(Presented by Academician I. N. Nazarov, 25 IV 1957)

As is known, the addition of halogens and hydrohalic acids to the simplest of the π -conjugated systems, butadiene-1,3, proceeds in the form of a primary act both at the 1,2 positions and at the 1,4 positions, with one or the other of these directions predominating, depending on the experimental conditions. In the theory of Ingold et al. this dual reactivity of divinyl has found the following explanation ⁽¹⁾.

“In reactions of π -conjugated systems two factors are manifested: the static factor of conjugation (the mesomeric effect) and its dynamic factor (the electromeric effect)” ⁽²⁾. The first factor is manifested in the molecule outside the reaction, the second—at the moment of reaction.

The **effect of static conjugation** is due to the predominance in the divinyl molecule outside the reaction of structures I and II over all the I–V and other structures ^(3,4) considered in the aforementioned theory in the quantum-mechanical description of the molecule by the method of localized pairs. In another, fundamentally identical ^(5,6) notation, it is due to the predominance of electron displacements IIa (I \leftrightarrow II) ^(1,7,8) over all possible IIa–Va and other displacements:

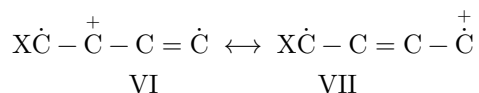


In other terms, the effect of static conjugation (mesomeric) is equivalently characterized also as follows. In a π -conjugated system “the p -orbital of the middle atom C_2 overlaps to an equal degree with the p -orbitals of both neighboring atoms” ⁽⁵⁾ (Fig. 1). “The density of π -electrons in all bonds is to a greater or

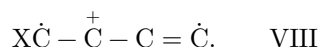
lesser extent equalized, and the difference between the bonds is smoothed out”⁽⁵⁾, namely: “the ordinary value of the C–C bond length, 1.54 Å, is decreased in butadiene to 1.46 Å. The lengths of the C=C bonds, on the contrary, are somewhat increased”⁽⁹⁾. All this also means that the “conjugation of double bonds—a factor reflected in the molecule outside the reaction”⁽²⁾—in the observed effect of static conjugation, supposedly, in a certain mesomeric state of the molecule. In this state of the divinyl molecule “atoms 1,4 have partially the character of free radicals”⁽⁴⁾; on them there occurs a concentration of electron density⁽²⁾, and a decrease in the covalency of these atoms^(1,7,10–12) occurs, which is what ensures the “increased reactivity of the 1 and 4 atoms”⁽²⁾, i.e., creates favorable conditions for attack of these atoms by the positive ion of an electrophilic reagent.

At the moment of this attack, the **dynamic part of the conjugation effect** comes into play (**the electromeric effect**)—

there occurs an “induction”⁽²⁾ of an electron through the readily polarizable system of conjugated bonds, in addition to the electron density already concentrated on this atom (owing to the static part of the conjugation effect); the relative weight of electromeric displacements of the type IIIa–Va, etc. (structures III–V, etc.) increases. This completes the addition, to atoms 1 or 4, of the positive ion X ($X = \text{H}^+, \text{Cl}^+, \text{Br}^+$), with the simultaneous formation, in Ingold’s terms⁽¹³⁾, and Baeyer’s⁽¹¹⁾, of a *mesomeric* carbonium ion, or, in Wheland’s terms⁽³⁾, of the corresponding resonance hybrid:



or, in another notation,



It is precisely the mesomerism of this carbonium ion which, according to the theory under consideration, determines the further dual course of the addition reaction. Ingold writes⁽¹³⁾: “In addition reactions to conjugated systems the intermediate carbonium ion is, of course, *mesomeric*, and therefore has two or more positions for neutralization in one particle at the final stage of addition” (in divinyl—positions 2 and 4). In works^(2,14–16) this presence of two centers of neutralization is explained with the aid of new terms: “natural center” (in ion VIII, atom 2) and “transfer of the reaction center of the molecule through the system of conjugated bonds” (in ion VIII, to atom 4). The term “transfer of the reaction center” emphasizes that it is unnecessary to assume the separate independent existence of particles VI and VII as isomers of the tautomeric process $\text{VI} \rightleftharpoons \text{VII}$ in order to explain the dual reactivity of conjugated systems*.

Figure 1. Overlap of p -orbitals in a conjugated system of π -bonds

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“Dual reactivity is ensured by the conjugated system”⁽²⁾, in butadiene-1,3 by the mesomeric state of a single particle—the ion VIII ($\text{VI} \leftrightarrow \text{VII}$), by the presence in it of π -conjugation and electron delocalization.

The theory considered rests on hypothetical assumptions about electron displacements which do not correspond to reality. Experimental data refute these assumptions.

An unquestionable experimental fact is the shortening of the interatomic distance of the single bond C–C in divinyl ($1.46 \pm 0.03 \text{ \AA}$) as compared with the C–C bond in ethane ($1.54 \pm 0.03 \text{ \AA}$). This shortening lies beyond experimental error. The discrepancy, however, in the results of measurements of the interatomic distance C=C in divinyl ($1.35 \pm 0.02 \text{ \AA}$) and in ethylene ($1.353 \pm 0.001 \text{ \AA}$, $1.34 \pm 0.02 \text{ \AA}$, 1.33 \AA) lies entirely within experimental error, and from the available data one can speak both of a lengthening and of a shortening of this distance⁽¹⁷⁾. But the data on vibrational frequencies, obtained with much greater accuracy than the data on interatomic distances, indicate precisely a shortening of the interatomic distance C=C in divinyl: the characteristic frequency of C=C in divinyl (1638 cm^{-1}) is substantially higher than in ethylene (1621 cm^{-1}); this excess lies beyond experimental error and means that in divinyl—

* “It is more correct to regard as tautomerism only the domain of phenomena predicted by Butlerov—the domain of equilibrium reversible isomerizations. Then another domain is delimited—the domain of phenomena of dual reactivity and the domain of transfer of the reaction center of a molecule as a result of resonance phenomena and of the particular case of resonance-hyperconjugation”⁽¹⁵⁾.

the C=C interatomic distance in divinyl is not less than in ethylene⁽¹⁸⁾, i.e., there is no basis for speaking of any mesomeric effect of static conjugation in divinyl of type IIa (I II).

According to the theory under consideration, this effect should be still more pronounced in diacetylene. However, the experimental data indicate its complete absence. Indeed, the C–C interatomic distance in diacetylene is sharply shortened, amounting to $1.36 \pm 0.03 \text{ \AA}$ as against $1.46 \pm 0.03 \text{ \AA}$ in divinyl and $1.54 \pm 0.03 \text{ \AA}$ in ethane. But at the same time the C C distance in diacetylene ($1.19 \pm 0.03 \text{ \AA}$), compared with acetylene ($1.205 \pm 0.008 \text{ \AA}$), is not only not lengthened but, beyond any doubt, shortened⁽¹⁷⁾, as is also evidenced by the

very considerable increase (by 209 cm^{-1}) in the vibrational frequency of the C C bond in diacetylene (2183 cm^{-1}) compared with acetylene (1974 cm^{-1})⁽¹⁹⁾.

The inadequacy of the quantum-mechanical scheme of Fig. 1 is already indicated by the very history of the appearance of these “dumbbells” (“figure-eights”) in the theory of π -conjugated systems. The “figure-eight” first appeared as a graphical representation of the results of simplified calculations of only one of the terms in the well-known expression, in polar coordinates, for the probability cloud of finding the single valence electron of hydrogen and hydrogen-like atoms in a p -state near the nucleus as a function of only one polar coordinate—the angle ϑ (“latitude”). The specific features of this case are the spherical symmetry of the field, a single valence electron, and the absence of the influence of an external field. In the theory under consideration, the “figure-eight” obtained in this way was transferred to the p -electrons of a carbon atom as a “ready-made element” and included in extremely simplified calculations of complex molecules with multiple bonds, the result of which, in particular, was the quantum-mechanical scheme of Fig. 1^(4,5,20–22). This transfer was made despite the fact that the carbon atom in the molecules under consideration lacks spherical symmetry of the central field, is acted upon by the field of neighboring atoms, and has four interacting valence electrons.

If the scheme of Fig. 1 reflected reality, then all C=C bonds in divinyl would have to be considered equivalent. However, as we have seen, the C–C interatomic distance in divinyl is closer to a single bond, while the C=C bonds are shortened. An analogous nonequivalence of the C C and C–C bonds is also found in diacetylene (see above).

It follows directly from the experimental data cited that one of the pairs of π -electrons in divinyl belongs to carbon atoms 1,2, and the other to 3,4. One of the most striking proofs of such localization of electrons along the bonds is the structure of diacetylene: the shortening in it of the C–C distance (1.36 \AA) to the length of the interatomic distance in a double C=C bond⁽¹⁷⁾ is not accompanied by the appearance of the vibrational frequency characteristic of it, since to ensure this frequency it is necessary for atoms 2,3 to possess a second pair of electrons (π -electrons), which in fact is not the case: the two pairs of π -electrons are strictly localized in the bonds of carbon atoms 1,2 and 3,4, providing full-valued ethylenic bonds (even more shortened and stronger).

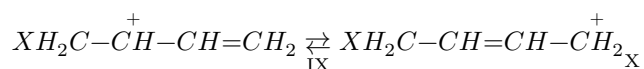
The interaction of these pairs of π -electrons with one another, confirmed by UV spectra⁽²³⁾, etc., leads to two results established above: 1) to compression of the single C–C bonds in the π -conjugated system without conversion of the single bond into a double one*; 2) to compression of the multiple bonds.

In the divinyl molecule its most electronized regions are the regions of carbon atoms 1,4 with methylene, not methine, groups, as evidenced by the higher vibrational frequencies of the methylene groups, especially in their antisymmetric vibrational state^(18,26). Naturally—

* Localization in the bonds 1–2 and 3–4 of the mutually interacting pairs of

π -electrons as if “from without” brings together the atoms of the C–C bond without the appearance between them of an additional

but the positive ion X of the reagent ($X = H^+, Cl^+, Br^+$) is directed into these regions of the molecule; becoming completely polarized in them, it adds to one of the terminal atoms of the system with the formation of the ion $XH_2C-\overset{+}{C}H-CH=CH_2$. This is the first stage of the addition reaction, proceeding in time. Addition of the positive ion occurs through the tearing away of a pair of π -electrons from the interrelated pairs of π -electrons of the conjugated system. This tearing away imparts to the remaining pair of π -electrons the corresponding impulse, reinforced by the greatly increased electronegativity of the carbon atom C^+ , which creates favorable conditions for the transition of IX into X. But the presence in X, at the end of the chain, of the strongly electronegative atom C^+ , in turn, under appropriate conditions favors the transition of X into IX, i.e., tautomerism of carbonium ions is established:



These are precisely two tautomeric ions, different in their chemical structure (in the order of bonds), and not one mesomeric or hybrid ion ($IX \leftrightarrow X$). Depending on the conditions of the reaction, addition of the negative ion (Cl^-, Br^-) may take place at species IX in position 2 (1-2 reaction) or at species X in position 4 (1-4 reaction).

From what has been said it is evident that the dual reactivity of divinyl–addition at positions 1,2 and 1,4—is fully explained by the separate existence in space of ions IX and X, different in their chemical structure, which in time tautomerically rearrange into one another and enter the reaction in its final stage—upon addition of the negative ion to divinyl.

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force interaction provided by the second pair of electrons (π -electrons), which is absent in bond 2-3 and which alone could have imparted to this bond values of its parameters characteristic of a double bond. The force constant of the central $C-C$ bond in diacetylene and dimethyldiacetylene is significantly (by more than 20%) reduced in comparison with the force constant of the $C-C$ bond of ethane, as is its vibrational frequency (^{24,25}).

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

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