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THE IONIZATION POTENTIALS OF BUTADIENE.

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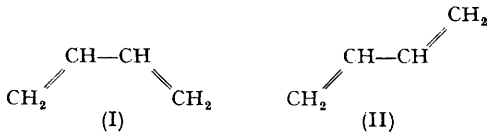
As a consequence of the interaction of its four π electrons, butadiene is expected to exist in two forms which may be designated *s-cis* (I) and *s-trans* (II) (Mulliken [1, 2]).



(I) (II)

Because of the different symmetry of these molecules, the selection rules for electronic transitions differ. In particular, the intra-valence-shell transition $N \rightarrow V_2$ is forbidden for *s-trans* but allowed for *s-cis*. In consequence, for *s-trans* $N \rightarrow V_1$ should be strong and $N \rightarrow V_2$ weak; while for *s-cis* the reverse should hold (Mulliken [1]).

Since the far ultra-violet absorption spectrum, described by Price and Walsh,[3] shows strong absorption for $N \rightarrow V_1$ (around 2100 A.), butadiene may be taken to be largely *s-trans* at room temperature. However, the absorption in the neighbourhood of 1700-1750 A., identified as $N \rightarrow V_2$, though weaker than that at 2100 A., is yet sufficiently strong to make it appear that an appreciable proportion of the butadiene molecules are in the *s-cis* form at room temperature. Mulliken [1] estimates 20 %.

More recently, Rasmussen, Tunnicliff and Brattain [4] have found that the 2200-2400 A. absorption is strongly temperature-dependent. The optical density increases with temperature. This suggests an equilibrium at room temperature between *s-cis* and *s-trans* molecules and that the proportion of the latter increases with temperature. As a consequence of coincidences between the observed Raman frequencies at −80° C. and the infra-red frequencies at room temperature, they conclude that at low temperatures butadiene is entirely *s-cis*, but predominantly *s-trans* at room temperature.

Price and Walsh [3] found two prominent Rydberg series both leading to the same limit, 9·02v. This is presumably the ionization potential of *s-trans* butadiene. Other, weaker, bands were present, but on the basis of the spectroscopic observations alone it was not possible to say whether these afforded any indication of an ionization potential for the *s-cis* form. The ionization potentials of butadiene have since been further studied by one of us (T.M.S.), using the electron impact method of Mackay.[5] The results obtained by the electron impact method are much less accurate than those determined by spectroscopic Rydberg series, but they have the great advantage of indicating clearly the *existence* of an ionization potential: used in conjunction with spectroscopic methods they form a very powerful tool. The experimental details of the electron impact investigations will be published elsewhere: here we wish to refer only to the results for butadiene.

The curve of ion current / accelerating potential, shown in the accompanying figure, exhibits a very peculiar anomaly which has hitherto not been observed for any other substance. Positive ions begin to appear

[1] Mulliken, *J. Chem. Physics*, 1939, **7**, 121.
[2] Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265.
[3] Price and Walsh, *Proc. Roy. Soc.*, 1940, **174**, 220.
[4] Rasmussen, Tunnicliff and Brattain, *J. Chem. Physics*, 1943, **9**, 432.
[5] Mackay, *Phil. Mag.*, 1923, **46**, 828.

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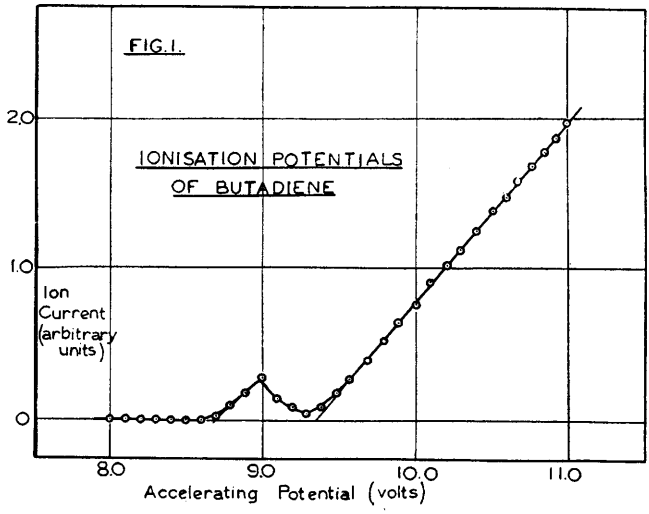
and give an increasing current with rising applied potential at a point corresponding to an ionization potential of 8·7 v. obtained by linear extrapolation. At rather higher values of the potential difference the ion current falls off and shows a minimum before rising again at a value somewhat above 9 v.

The curve suggests the existence of two butadiene ionization potentials in the range 8·5 to 9·5 v. The upper (~ 9·3 v.) doubtless corresponds to



the value found by Price and Walsh: electron impact values are often a few tenths of a volt higher than spectroscopic values. The lower ionization potential of ~ 8·7 v. might plausibly be ascribed to *s-cis* butadiene: its discovery prompted a re-examination of the weak bands of the butadiene electronic spectrum.

It is possible to arrange certain of these weaker bands into the following Rydberg series

$$\nu_0^n = 70606 - \frac{n}{(m + 0{\cdot}90)^2}. \quad . \quad . \quad . \quad (1)$$

The series is plausible since there is very good agreement between the observed and calculated frequencies (Table I), as many as six members being observed, and since the intensity decreases regularly in the passage to higher members. The limit corresponds to 8·71 v. Taken alone, the spectroscopic evidence would probably justify acceptance of this Rydberg series; in conjunction with the electron bombardment results, we believe it provides strong support for the existence of an ionization potential of the above value. If so, 8·71 v. must be the first ionization potential of *s-cis* butadiene.

TABLE I.—TABLE SHOWING THE OBSERVED AND CALCULATED FREQUENCIES OF THE BANDS OF SERIES (1).

n.	$\nu_{obs.}$ cm.$^{-1}$.	$\nu_{calc.}$ cm.$^{-1}$.
3	63372	63391
4	Obscured by 1515 doublet	66036
5	67451	67454
6	68299	68301
7	68850	68848
8	69216	69221
9	69500	69486

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The $n = 3$ member of series (1) appears as a doublet. The $n = 2$ member of the series should fall in the 1700-1750 A. region: that is, it is plausible to identify the $N \rightarrow V_2$ transition as the first member of the series ($\nu_{max.} = 57800$, $\nu_{calc.} = 57558$ cm.$^{-1}$). This rather supports the assignment of the series to *s-cis* butadiene, since the $N \rightarrow V_2$ absorption is known to be due to the *s-cis* form and since it is a general rule that an $N \rightarrow V$ transition of an electron may also be classified as the first member of a Rydberg series for that electron. Examples are to be found in the spectra of the chloroethylenes (Walsh [6]), of aldehydes (Walsh [7]), of hexatriene (Price and Walsh [8]) and in the various derivatives of acetylene (Price and Walsh [9]). Similarly it is probable that the 2100 A. region of butadiene may be classified not only as the $N \rightarrow V_1$ transition but also as the first member of one of the Rydberg series found for *s-trans* butadiene.

There remains the difficulty of the minimum in the curve of ion current / accelerating potential. Such a minimum has not previously been observed in electron impact work with a large number of substances. If the vapour consisted of an equilibrium mixture of *s-cis* and *s-trans* isomers a continually increasing current would be expected, though a break would occur at about 9·1 v., corresponding with the appearance of *s-trans* positive ions. It appears that between the two ionization potentials either *s-cis* positive ions are being removed or are not being formed in the expected number.

We are inclined tentatively to explain the minimum as due to the second of these causes. The four π electrons of butadiene occupy in pairs orbitals χ_1 and χ_2. The ionization potentials here discussed refer to the positive ion $\chi_1^2\chi_2$. Before the ion current curve begins to fall off, presumably only a χ_2 electron is excited on collision with a bombarding electron. Suppose, however, an energy level of the χ_1 electrons lies between the *s-cis* and *s-trans* χ_2 ionization potentials. Then when this energy value is reached, some of the collisions of the *s-cis* molecules with electrons lead not to excitation and ionization of χ_2 electrons, but to excitation of χ_1 electrons. It is true that excitation of a χ_1 electron may still lead to χ_2 removal, as a result of a process of auto-ionization; but it also facilitates conversion of *s-cis* to *s-trans* molecules. The net result is therefore that some collisions which previously resulted in χ_2 ionization now result instead in the formation of *s-trans* molecules. The excited *s-trans* molecules will not form ions because the minimum *s-trans* ionization potential is higher than the energy corresponding to the falling part of the curve. The current therefore falls off. The *cis* V_3 state might possibly be available as a suitable energy level for this explanation to hold.

Discussion.

It may be significant that the difference (0·31 v.) of the ionization potentials found for *s-cis* and *s-trans* butadiene is just the amount by which the ionization potential of *cis* dichloroethylene (9·61 v.) is less than that of *trans* dichloroethylene (9·91 v.). The dichloroethylenes, of course, possess resonance structures giving the hybrid something of a conjugated diene form.

The results of Rasmussen *et al.*[4] indicate an appreciable difference in stability between *s-cis* and *s-trans* butadiene. The present work shows that the ground states of the least strongly bound π electrons in the two forms differ by as much as 0·3 v.

It might be expected in consequence that the $N \rightarrow V_1$ transition of the *s-cis* form might appear at a much longer wavelength than that of

[6] Walsh, *Results in course of publication.*
[7] Walsh, *Results in course of publication.*
[8] Price and Walsh, *Results in course of publication.*
[9] Price and Walsh, *Results in course of publication.*

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the *s-trans* form. This is not necessarily so, however, for in the case of the dichloroethylenes the *trans* ionization potential is 0·3 v. higher than that of the *cis* and yet the *trans* $N \rightarrow V$ transition occurs about 0·15 v. *lower* than that of the *cis* ($\lambda_{max.}$ = 1900 and 1950 A. for *cis* and *trans* respectively). If *s-cis* butadiene has an $N \rightarrow V_1$ transition falling about 50 A. away from that of *s-trans*, the latter with its greater intensity would easily mask the former. Presumably the difference in energy of the excited states in *cis* and *trans* forms compensates for the difference in ground state.

It has always been difficult to understand the appearance of absorption in cyclopentadiene and cyclohexadiene at relatively long wavelengths compared with the open chain dienes. In order to explain it, Mulliken invoked the theory of hyperconjugation. According to this, weak conjugation could occur between unsaturation electrons and the electrons in C—H bonds. At first the effect was supposed to leave unchanged the energy of the ground state but to depress the energy of the excited V_1 state. Price and Walsh [10] pointed out that this was quite inconsistent with the observed spectra of the cyclic dienes: *all* the electronic bands right up to and including the ionization potential suffered comparable shifts. The theory was later revised (Mulliken, Rieke and Brown [11]): hyperconjugation was no longer supposed to affect the V_1 upper state, but to raise the ground state. Even in this form, there was experimental evidence not in accord with the theory (see, for example, Bateman and Koch [12]).

The problem arose essentially because of the comparison of the cyclic dienes with the spectra of (largely) *s-trans* butadiene. It is obviously more satisfactory to compare the absorption with that of *s-cis* butadiene. Accepting the present results, we then have a lowering of 8·71 − 8·58 v. = 0·13 v. for the ionization potential of cyclopentadiene relative to *s-cis* butadiene. This is quite within the range we should expect by a simple charge transfer effect consequent upon the addition of a CH_2 group. The further lowering ~0·2 v. in passing to cyclohexadiene may be largely explicable as due to a further charge transfer from the second CH_2 group. Alternatively, it may in part be due to a widening of the angle between the double bonds and the outer single bonds, relative to cyclopentadiene. These results suggest that the changes in the ground states of the cyclic dienes relative to the *s-cis* open chain dienes do not require the invocation of any such theory as that of hyperconjugation: they are explicable simply as charge transfer and strain effects.

A considerable part of the abnormal red shift of the first absorption of cyclic dienes may be explained as due to a ground state shift consequent simply upon the *s-cis* arrangement of the conventional double bonds and not due to the nature of attached groups. Bateman and Koch [12] point out that the heat of hydrogenation of cyclohexadiene is much the same as that of open chain dienes. They therefore criticise any theory, such as that of charge transfer, which explains the red shift of cyclohexadiene as due to a change in the ground state. The criticism, however, is not valid. It would be valid if we were dealing with molecules containing a *single* pair of unsaturation electrons (thus Price and Tutte [13] show the correlation that exists between heats of hydrogenation and $N \rightarrow V$ frequencies for the alkyl ethylenes); but for conjugated dienes the electrons occupy *two* ground state orbitals and whereas the ionization potential refers to only one of these orbitals, the heat of hydrogenation depends upon the energies of both orbitals. In order to correlate the heats of hydrogenation of conjugated dienes with their ionization potentials, we

[10] Price and Walsh, *Proc. Roy. Soc.*, 1941, **179**, 201.
[11] Mulliken, Rieke and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41.
[12] Bateman and Koch, *J. Chem. Soc.*, 1944, 600.
[13] Price and Tutte, *Proc. Roy. Soc.*, 1940, **174**, 207.

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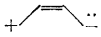
need to know the energy levels of each of the two ground state occupied orbitals.

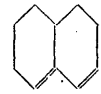
The present results clarify somewhat the facts relating to the abnormal red shift of cyclic diene absorption. Two problems remain, however. First, why should the *cis* arrangement of the double bonds cause a red shift of the ground states of dienes ? Second, what is the cause of the $N \rightarrow V_1$ shift of cyclic dienes relative to *s-cis* butadiene ?

As regards the first of these problems, Price and Walsh [3] have already pointed out that the lower ionization potential of *s-cis* dienes relative to *s-trans* may be due either to repulsion between the double bonds or to resonance in the *s-cis* form to structures involving interaction between electrons on the outer carbon atoms—*e.g.* III. The latter increase the resonance energy not only directly but also indirectly by holding the four π electron distributions in a more nearly planar condition. Such a question of planarity may also affect the states of the cyclic dienes, where some of the carbon atoms of the ring have trigonal valencies and some tetrahedral.



(III)

As regards the second problem, Price and Walsh [10] have stressed that the $N \rightarrow V_1$ shifts of cyclic dienes relative to *s-trans* butadiene are not much more than those normally associated with ground state changes of the magnitude shown by the ionization potentials. The abnormality thus seems to lie more in the $N \rightarrow V_1$ location for *s-cis* butadiene than for the cyclic dienes. The $N \rightarrow V_1$ red shift seems to be shown by all molecules possessing an *s-cis* diene structure incorporated in a six-membered ring.[12, 14] Conversely, dienes with an *s-trans* arrangement do not seem to show this shift. We are indebted to Dr. Koch for pointing out that molecules of the type (IV) which have an *s-trans* arrangement in a cyclic structure, yet have a "normal" absorption spectrum. The abnormality of *s-cis* butadiene must be explained as due to a peculiarity of the V_1 upper state, possibly consequent upon the open-chain nature of the molecule.



(IV)

The authors desire gratefully to acknowledge their indebtedness to Dr. W. C. Price for his encouragement and help throughout the work that has led to the publication of this paper ; and also to Dr. H. P. Koch who has given them many constructive criticisms of great value.

Summary.

Evidence based upon the vacuum ultra-violet spectrum and electron impact determinations of ionization potentials is presented to show that butadiene exists in two forms, *s-cis* and *s-trans*, at room temperature. The *s-cis* form has a minimum ionization potential of 8·71 v. as against 9·02 v. for the *trans* isomer. This fact makes it possible to explain the low ionization potentials of cyclopentadiene and cyclohexadiene without recourse to the theory of hyperconjugation.

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Cambridge.

[14] Booker, Evans and Gillam, *J. Chem. Soc.*, 1940, 1453.

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