

Absorption Spectra of Dimer Cations

Part 1.—Olefins

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The absorption spectra of γ -irradiated glasses at 77 K containing cyclohexene, butadiene and penta-1,3-diene have been studied. The effects of warming and recooling and of concentration show that the bands can be assigned to monomeric and dimeric radical cations (M^+ and M_2^+). Assignments of the corresponding spectra of a number of olefins obtained by other workers are discussed.

Two helium atoms do not normally combine, but they can do so if one of them is ionized or excited. He_2^+ has the electronic structure— $(1s\sigma_g)^2(1s\sigma_u)$: the two bonding electrons outweigh the one anti-bonding electron. Though it has not been observed, He_2^+ should have a continuous absorption corresponding to the allowed transition to the repulsive state, $(1s\sigma_g)(1s\sigma_u)^2$, in addition to transitions correlated with those of the separate atoms. This absorption can also be described as taking place between states with wave-functions— $\psi(A^+)\psi(B) \pm \psi(A)\psi(B^+)$ —and so is termed a “charge-resonance” band, where A and B are the two atoms. These arguments apply equally to the other inert gases and also to stable molecules (M), provided that the highest occupied orbitals can overlap: this criterion is fulfilled in the numerous olefins and aromatics, which have many or all of their atoms lying in one plane and in which the π orbitals are the highest filled orbitals. The species, M_2^+ , should be stable with respect to dissociation and should have a strong, broad, charge-resonance absorption. The name, dimer cation, for M_2^+ , is used in preference to cation dimer which suggests $(M^+)_2$. Such ions of all the inert gases and N_2 , CO, O_2 are well known, as are the corresponding bound excited species, M_2^* , of helium and the aromatic hydrocarbons (excimers), but only recently have dimer cations of e.g., naphthalene been detected by e.s.r.¹ and absorption spectroscopy.² The e.s.r. spectra show that the ions have a sandwich configuration, like that of the excimers.

Organic ions are easily produced by radiolysis of glassy solutions at 77 K.^{3, 4} Methods of identification of cations, anions and radicals are well developed;⁴ cations are best studied in halide glasses where positive charge may be transferred to the solute, while electrons are trapped in the solvent by dissociative attachment: a mixture of isopentane and n-butyl chloride (in equal volumes) was used in this work. Here, both monomer and dimer cations of cyclohexene, butadiene and penta-1,3-diene have been found and it is argued that many of the cationic olefin species found by other workers^{5, 6} are dimeric. Similar results have been obtained with aromatic hydrocarbons^{2, 7} and, together with theoretical calculations, will be reported in later papers. All these species are characterized by the strong, structureless, charge-resonance absorption in the visible or near infra-red: presumably the olefins also form “sandwiches”, i.e., there is σ interaction of the π electrons.

EXPERIMENTAL

Solutions were placed in cylindrical quartz cells—about 20 mm diam., 12 mm between the optical surfaces (made from Suprasil discs). Some samples were degassed though this was not found to affect the results in halide glasses. They were irradiated with Co^{60} γ -rays at 77 K (dose rate, 90 krad h^{-1}) and then transferred to a quartz Dewar vessel with flat windows which fitted the cell so that the light beam did not pass through liquid nitrogen. Absorption spectra were measured in a Unicam SP700 spectrophotometer; "blanks", obtained by warming to room temperature and recooling the samples, were subtracted from the measured spectra. In early work,² dimer cations were produced in some cases by allowing the samples to warm up slightly, until a colour change was observed, and then re-cooling. This procedure was difficult to control and often gave a cracked glass. It was found that transferring the samples to liquid oxygen for periods of minutes or hours produced better results.

Isopentane and *n*-butyl chloride (B.D.H.), were passed through columns of activated silica gel until they did not absorb above 230 nm. Cyclohexene (Hopkin and Williams), butadiene (Matheson), trans-penta-1,3-diene (Fluka) and bicyclo-[2,2,1]-hepta-2,5-diene (norbornadiene; Koch-Light) were used without further purification.

RESULTS

The absorption spectra of the irradiated pure solvent and some cyclohexene solutions are shown in fig. 1. The pure solvent became brown, dilute solutions green, concentrated ones, blue. When a 5×10^{-2} M solution was placed in liquid oxygen for 15 min the colour changed to blue: the $2.33 \mu\text{m}^{-1}$ band disappeared leaving

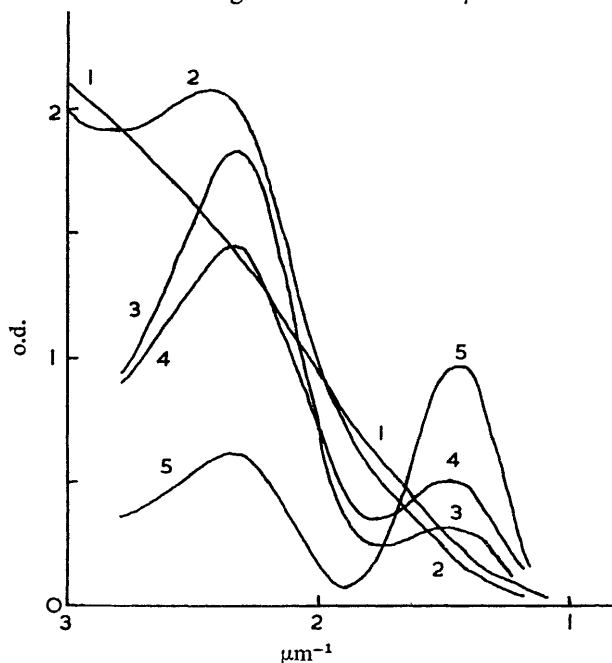


FIG. 1.—Absorption spectra of irradiated cyclohexene solutions in 1 : 1-isopentane + *n*-butyl chloride; dose 270 krad. Curve 1, pure solvent; 2, 10^{-2} M; 3, 5×10^{-2} M; 4, 10^{-1} M; 5, 5×10^{-1} M.

that at $1.44\ \mu\text{m}^{-1}$. Butadiene and penta-1,3-diene showed a similar effect of concentration; some results for dilute and concentrated solutions are given in table 1; intermediate concentrations gave spectra of intermediate character. Butadiene solutions were brown (dilute) and yellow-green (concentrated). The pentadiene solutions were red-brown and green respectively; warming produced a transitory green colour in the first case, no immediate change in the second. A 5×10^{-2} M solution of norbornadiene gave a blue colour due to a single band at $1.55\ \mu\text{m}^{-1}$, and absorption increasing again slowly between 2.0 and $2.5\ \mu\text{m}^{-1}$; an attempt to obtain the anion by irradiation of a solution in 2-methyl tetrahydrofuran was unsuccessful.

TABLE 1.—ABSORPTION BANDS OF OLEFINS IN 1 : 1 ISOPENTANE; *n*-BUTYL CHLORIDE AFTER 270 krad IRRADIATION AT 77 K

| | ν^a μm^{-1} | ν^b μm^{-1} | ν^a μm^{-1} | concentration M | optical density | assignment ^d |
|-----------------|-------------------------------|-------------------------------|-------------------------------|--------------------|-------------------|-------------------------|
| cyclohexene | 1.27 | 1.41 | 1.44 | see fig. 1 | | d |
| | 1.82 | | 2.33 | | | m |
| | 3.03 | | | | | |
| butadiene | | 0.83 | 0.83 | 0.05 | 0.025 | d |
| | | | | 0.66 | 0.19 | |
| | | — | (1.55) | 0.05 | 0.11 | d |
| | | | | 0.66 | 0.27 | |
| | 1.75 | 1.74 | 1.77 | 0.05 | 0.51 | m |
| | | | | 0.66 | 0.45 | |
| | | 2.35 | 2.33 | 0.05 | 1.02 | d |
| | | | | 0.66 | 1.44 | |
| | 2.47 | (2.6) | 2.58 | 0.05 | 1.13 | m |
| | | | | 0.66 | 1.15 | |
| penta-1,3-diene | | 0.80 | 0.79 | 0.1 | — | d |
| | | | | 1.0 | 0.34 | |
| | | | 1.50 | 0.1 | 0 | d |
| | | | | 1.0 | 0.09 | |
| | | | 1.85 | 0.1 | 0.80 | m |
| | | | | 1.0 | 0.09 | |
| | | | 2.22 | 0.1 | 0.59 | d? |
| | | | | 1.0 | 1.93 | |
| | | 2.30 | 2.32 | 0.1 | 0.66 | d? |
| | | | | 1.0 | 1.85 | |
| | | | 2.74 | 0.1 | 0.92 ^e | m |
| | | | | 1.0 | 0.68 | |

() indicates a shoulder. ^a calculated from data of Al-Joboury and Turner, see text; ^b Shida and Hamill; ^c this work; ^d m = monomer, d = dimer; ^e measured at 0.2 M.

Some of Shida and Hamill's data ^{5, 6} are shown in table 1; where observations overlap there is good agreement. From fig. 1, it appears that the solvent absorption is present at low concentrations; after a rough correction is made for this, the optical density ratio of the two peaks (1.44/2.33) is proportional to concentration (except that at 10^{-2} M the $1.44\ \mu\text{m}^{-1}$ peak is not observed). Except that our measurements extend to lower concentrations, the concentration dependence of the long wavelength peak is similar to that found by Shida and Hamill.⁶ These authors do not record the $2.33\ \mu\text{m}^{-1}$ peak; it is obscured by a band due to the solvent (sec-butyl chloride); our solvent does not give a peak in this region (fig. 1).

DISCUSSION

The behaviour of the olefins is similar to that of the aromatic hydrocarbons^{2, 7}; the assignments (table 1) are based on the effects of concentration and of warming. The long wavelength bands of other olefins^{5, 6} are probably also due to dimers. A plot of dimer cation yield against concentration should show an initial positive curvature: this can be seen in our results for cyclohexene and in Gallivan and Hamill's for 2-methyl-pent-1-ene.

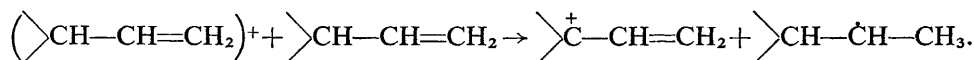
For transitions from lower-energy orbitals to the half filled orbital, the positions of their 0—0 bands (not the maxima) of the monomeric ions in the gas phase can be calculated from the ionization potentials of the orbitals obtained by photo-electron spectroscopy⁹; results are given in table 1. For butadiene, agreement with both observed monomer bands is satisfactory; in the second case, this is accidental since, if both are $\pi \rightarrow \pi$ transitions, the upper state involves an anti-bonding orbital. For cyclohexene, the situation is less clear and Shida and Hamill's assignment of the long wavelength band to a monomer $\sigma \rightarrow \pi$ transition must be considered. To a first approximation, σ orbitals can be classified as $p\sigma$ and $s\sigma$; transitions from $p\sigma$ to π are forbidden, $s\sigma$ to π are allowed; because of the s — p splitting in the carbon atoms $s\sigma$ will lie well below $p\sigma$. In the planar $\text{CH}_3\cdot$ radical, $s\sigma$ and $p\sigma$ have different symmetries and so do not mix: in olefins this is not true but the extent of mixing is probably small, so that one expects a weak transition (mainly $p\sigma \rightarrow \pi$) at long wavelengths, a strong one at short wavelengths. This view is supported by the observation that $\sigma \rightarrow \pi$ transitions in a number of diatomic molecules (OH , NH , CH , N_2^+ , CO^+) are weak, e.g., the oscillator strength of the N_2^+ , $A^2\Pi_u - X^2\Sigma_g^+$, bands is $\sim 2 \times 10^{-3}$.¹⁰ Extinction coefficient measurements have not been made but from the data for hex-2-ene,⁶ an oscillator strength $> 4 \times 10^{-2}$ can be estimated.

In our work on aromatic compounds,^{2, 7} and the extensive e.s.r. studies of solutions of negative ions, no dimer anions have been detected: this is puzzling, as the arguments for the stability of dimer cations apply equally to the anions. However, in agreement with this, Shida and Hamill⁵ find no long-wavelength absorption in the di-olefin anions. If the $\sigma \rightarrow \pi$ assignment were correct, then there should be such a band in the anions. Also, they found a difference in the effect of substituents in butadiene on anion and cation spectra: this is explained by our assignment. Both mono- and di-olefins^{5, 6} show a red shift of the long wavelength cation band with increasing substitution, especially with substitution of methyl for hydrogen close to the double bond. This is easily understood as a steric effect if this is the charge resonance band, the position of which will depend on the overlap of the π -orbitals of the two molecules.

The theory of the monomer ion $\pi \rightarrow \pi$ absorptions of the diolefins has been discussed⁵; the corresponding absorption of a mono-olefin should be at very short wavelengths—approximately the same position as the $\pi \rightarrow \pi$ absorption of the neutral molecule (2β in the Hückel approximation—experimentally $\sim 5.5 \mu\text{m}^{-1}$ in ethylene). However, this assumes that the atoms surrounding the double bond remain planar, whereas the first Rydberg state of ethylene is twisted 26° out of plane.¹¹ This state should resemble the cation, C_2H_4^+ , for which Mulliken predicted a twist of about 30° .¹² But for the π -bond, the neutral cyclohexene molecule would tend to take up a configuration like that of cyclohexane. If this occurs in the cation, the $\pi \rightarrow \pi$ absorption should appear at $2\beta \cos 60^\circ = \beta$; also, β will be reduced by the increase of bond length on ionization. Assignment of the $2.33 \mu\text{m}^{-1}$ band to the $\pi \rightarrow \pi$ transition of a twisted monomer cation now appears plausible: the absence of this band in the dimer must be due to the retention of planarity. Shida and Hamill⁶

did not observe cation bands in this region, partly because of the high concentrations and the solvent absorption, but in any case, the other olefins may absorb at shorter wavelengths; the one exception was tetramethyl-ethylene ($2.74 \mu\text{m}^{-1}$): in this molecule, overcrowding will not only reduce the stability of the dimer (absorption at $1.15 \mu\text{m}^{-1}$) but also assist the twisting of the monomer.

Mono-olefins containing a $-\text{CH}=\text{CH}_2$ group do not give visible absorption bands though they do scavenge positive charge, presumably because of further reaction.⁶ The most likely reaction appears to be hydrogen atom transfer,



Shida and Hamill⁶ think this unlikely on energetic grounds, but they consider only the formation of an allyl radical and an unconjugated carbonium ion, whereas the above reaction is more favourable energetically. Smith and Pieroni¹³ have found e.s.r. evidence for such reactions in terminal and other olefins. They do not observe e.s.r. spectra of dimer cations (though they note the blue or green colours of olefins irradiated in the glassy state), but they studied only the pure olefins where efficient charge transfer⁸ leads to a considerable amount of ion recombination. No such reaction is expected in butadiene, but we find an extra peak in the pentadiene spectrum (table 1): also the absorption in the region of the 2.22 and $2.32 \mu\text{m}^{-1}$ peaks (which are only just resolved) is very strong. This suggests that a reaction like the above is occurring leading to an allyl radical (which should only absorb weakly in the visible region) and a pentadienyl cation. Related dienyl cations absorb in the region $2.35\text{--}2.55 \mu\text{m}^{-1}$ ¹⁴ so that the assignment of either the 2.32 or $2.22 \mu\text{m}^{-1}$ peak to the pentadienyl ion appears reasonable.

Norbornadiene was studied in the hope of obtaining evidence of an intramolecular charge resonance interaction. An e.s.r. study¹⁵ shows that the anion does behave in this way: the visible spectrum was not studied but the solutions appeared blue.¹⁶ The assignment of the $1.55 \mu\text{m}^{-1}$ band of the cation to a charge resonance transition appears reasonable since the overlap integral of p orbitals on the "non-bonded" carbon atoms is 0.083 (cf. 0.25 for $p\pi$ overlap in the double bond).⁷ Though the absorption was 50% stronger than that of a cyclohexene solution at the same concentration, we cannot rule out an intermolecular interaction.

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