198. Mode of Proton Addition to Conjugated Double Bonds.

By Albert Wassermann.

The light absorption and electrical conductance have been measured of vitamin-A acetate, a polyene with five conjugated double bonds, in benzene without and with trichloroacetic acid. The polyene is protonated in the presence of the acid; some information about the structure of the carbonium ion can be obtained.

In previous papers ¹⁻³ the proton transfer from trichloroacetic acid to nine conjugated polyenes has been investigated, but in most cases the structure of the resulting carbonium ions has not been specified. It is now shown that another polyene, vitamin-A acetate, containing five conjugated double bonds, accepts protons, under conditions similar to those in the earlier experiments, and that the electronic spectrum of protonated vitamin-A acetate enables one to decide whether the proton goes to the middle part of the conjugated system or to its ends.

It is assumed that the proton transfer withdraws two π electrons from the conjugated double bonds and forms a new methylenic group as in the protonation of aromatic hydrocarbons.⁴

The product from trichloroacetic acid and vitamin-A acetate, prepared as specified below, is blue and characterised by a light absorption peak at 650 m μ . That vitamin-A acetate, or the vitamin itself, can be converted into deeply coloured substances is known,

¹ Wassermann, J., 1954, 4329.

² Idem, J., 1955, 581.

³ Idem, J., 1958, 1014.

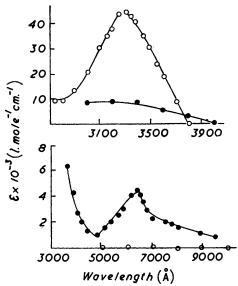
⁴ See, e.g., Dalinga, Mackor, and Verrijn Stuart, Mol. Phys., 1958, 1, 123, where are to be found references to earlier work.

the Carr-Price reaction, for instance, having been used for the colorimetric determination of the vitamin in biological materials.⁵ It is not known, however, whether the previously described coloured derivatives of vitamin-A are similar species to the carbonium-ion pairs which form the subject of this paper.

EXPERIMENTAL

The purifications and technique have been described. Vitamin-A acetate, m. p. 57°, was recrystallised from methanol. Most of the spectrophotometry was done with a special all-silica cell, of small optical path-length, 0.0944 cm., suitable for relatively concentrated solutions.

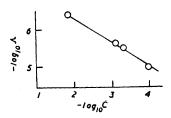
Fig. 1. Light absorption of vitamin-A acetate in benzene solution at 20°.



Concn. of vitamin-A acetate = 1.84×10^{-4} to 1.50×10^{-8} mole/l. \bigcirc = No acid. \blacksquare = 0.920m-Trichloroacetic acid.

⁶ Reid, J. Amer. Chem. Soc., 1954, 76, 3264.

Fig. 2. Molar electrical conductance, Λ , of ion pairs formed by proton transfer from trichloroacetic acid to vitamin-A acetate.



Benzene solution, $25 \cdot 0^{\circ}$. Ordinate: $-\log_{10} \Lambda$ (Λ in l. mole⁻¹ ohm⁻¹ cm.⁻¹); abscissa: $-\log_{10} c$ (e is concn. of ion pairs in mole l.⁻¹). The solution was $1 \cdot 00$ M with respect to trichloroacetic acid.

This is important because the rate of change of the optical densities, owing to a reaction with molecular oxygen, increases with decreasing polyene concentration. Back extrapolation of optical densities and of electrical conductances to the time of mixing was carried out.¹⁻³ The optical densities of solutions containing protonated vitamin-A acetate depend also on the intensity of illumination, this photochemical effect probably being similar to that with other carbonium ions,⁶ so all experiments were done in diffuse daylight of approximately equal intensity and the time of exposure to the light of the spectrophotometer (Unicam S.P. 500) was as short as possible.

Results.—The light absorption of vitamin-A acetate (Fig. 1) is markedly altered on addition of trichloroacetic acid, owing to proton-transfer. The equilibrium constant, K, relating to the proton uptake was obtained by plotting $\log K'$ (K' defined as in ref. 1) against trichloroacetic acid concentration and by extrapolating to zero concentration; K was so estimated to be 0.10 ± 0.02 l./mole in benzene at 20° . In these experiments the highest acid concentration was 3.96 moles/l. [here and below all concentration of trichloroacetic acid relate to the stoicheometric molecular weight]; at about half this concentration the optical density at 6500 Å had reached its limiting value. Measurements with different polyene concentrations were carried out, and the $\log K'$ values were extrapolated in each case to $[CCl_3 \cdot CO_2H] = 0$. The results of these

⁵ See, e.g., Gstirner, "Chem. Phys. Vitaminbestimmungsmethoden," Enke, Stuttgart, 1950; Moore, "Vitamin A," Elsevier, Amsterdam, 1957, chap. 7.

tests indicated that only one acid molecule reacts with the carbon–carbon double bond of the polyene. The proton-transfer leads to electrically conducting species. In calculating specific conductances a correction was applied which took care of the small specific conductance of the acid without the polyene. The concentration of the protonated species, c, was calculated from stoicheiometric concentrations with the help of the results of the equilibrium measurements. The linear $\log \Lambda$ - $\log c$ relationship (Fig. 2) is similar to that previously observed; $^{1-3}$ also the absolute values of Λ for protonated carotene, azulene, and vitamin- Λ acetate are of the same order of magnitude. Experiments with dioxan, which acts as a competitive proton acceptor, were carried out, as in those described by Fig. 5 in refs. 1 and 3 and by Table 2 in ref. 2. It could thus be established, as before, $^{1-3}$ that the proton transfer from trichloroacetic acid to the polyene is reversible, within an accuracy of $\pm 20\%$.

DISCUSSION

The equilibrium measurements make it probable that only one proton is transferred to the system of five conjugated double bonds of vitamin-A acetate. A second proton may be transferred to the carbonyl oxygen of the ester grouping, but as the carbon-oxygen bond is not conjugated with the other double bonds, which are responsible for the electronic spectra here considered, protonation of oxygen need not be taken into account.

In the transfer of one proton to the carbon-carbon double bonds four pairs of mesomeric ions can be formed. Reaction with $C_{(10)}$, for instance, leads to a species the limiting resonance structures of which are shown in (I). The numbers assigned to the ten carbon atoms are the same as those in the first column of the Table, which refers also to protonated species in which the new methylenic grouping is in the other positions 2, 3, 9. One could suggest that the rate of these proton-transfers depends exclusively on the energy of the relevant transition state, which is influenced by the resonance energy, R, the π -electron localisation energy, E, or the electron density, D, of the reaction centres; and that an estimate of the R, E, or D values, which correspond to proton uptake in the 1-, 2-, 10-positions would enable one to predict the structure of the protonated species. This method is not adopted here because the dielectric constant of the solvent, benzene, is low, and therefore the proton transfer involves the whole bulky trichloroacetic acid molecule, a hydrogen-bonded dimer, rather than protons which were already dissociated before the collision with the acceptor. In this situation the relative rate of protonation may depend not only on the energy, but also on the entropy of activation, effects of the latter kind being difficult to predict in this reaction.

The structure of protonated vitamin-A acetate is deduced here with the help of a simple free-electron treatment of mesomeric ions, which is based on a knowledge of λ_1 , the long-wavelength peak of the electronic spectrum and on ⁷

$$\lambda_1 = (8mc/h)L^2/(N+1)$$
 (1)

where m is the mass of the electron, c is the velocity of light, h is Planck's constant, L is the length of the chromophore, and N is the number of π electrons. Protonated polyenes are like asymmetric cyanine dyes 8,9 in that the limiting resonance structures are not identical, and therefore eqn. (1) gives merely an upper limit of λ_1 . The correct expression can be obtained 7,9 if the π electrons are considered to be placed in a one-dimensional potential having a sine-curve periodicity, but in general the numerical value of the potential is not known.

The four pairs of mesomeric vitamin-A acetate ions, referred to in the Table, are characterised by different L and N values. In order to gain information about the position of the new methylenic grouping, these parameters are estimated and introduced in (1), and

⁹ Kuhn, Helv. Chim. Acta, 1948, **31**, 1441; 1949, **32**, 2247; Chimia, 1955, **9**, 237.

⁷ Kuhn, J. Chem. Phys., 1949, 17, 1198.

⁸ Brooker, Rev. Mod. Physics, 1942, 14, 275. The term limiting resonance structure is used here as in ref. 6; cf. also Pauling, Proc. Nat. Acad. Sci., 1939, 25, 577.

the upper limit of λ_1 , so obtained, is compared with the experimentally observed light absorption peak, shown in the lower part of Fig. 1 (these considerations relate to the wavelength of the peak; light-absorption intensities are not discussed here). The chromophor lengths were calculated from eqn. (2) (cf. Kuhn^{7,9})

$$L = Xl_1 + 2l_2$$
 (2)

where X depends on the position of the new methylenic grouping, and l_1 and l_2 are taken to be 1.39 and 1.50 Å. These values are probably somewhat too large, but as only upper

limits of λ_1 are calculated, the conclusions are not affected. If l_2 is also taken to be 1.39 Å, λ_1 for protonation in the 1- or the 10-position becomes 3% smaller. The figures in the last

Proton taken up by carbon atom no.	No. of formal double bonds in mesomeric part of protonated species	X or N *	L (Å) *	No. of ordinary conjugated double bonds in protonated speces	$\lambda_1 \times 10^{-8}$ in Å (upper limits calc. from 1)
1 or 10	4	8	14.1	0	7.30
2 or 9				4	
3 or 8	3	6	11.3	0	6.04
4 or 7	1	2	5.78	3	3.67
5 or 6	2	4	8.56	${f 2}$	4.84

^{*} These parameters relate to the mesomeric part of the protonated species.

column of the Table show that only the λ_1 value in the first line relating to 1- or 10-addition is larger than the experimental figure of 6500 Å. If the proton is transferred to the 2or the 9-position, a mesomeric ion is not formed, the resulting carbonium ion containing four conjugated double bonds of the same type as those in the polyene before protonation. Such double bonds are also present in the species formed by 4- or 7- and 5- or 6-addition, which is indicated in col. 5 of the Table. These double bonds, in contrast to the formal double bonds in the mesomeric part of the protonated polyene, cannot give rise to lightabsorption peaks above 3000 Å.10 The experimentally determined light-absorption curve makes it probable, therefore, that the proton uptake by vitamin-A acetate leads to the mesomeric ion with the maximum number of formal double bonds.

Discussions with Professors D. P. Craig and H. Kuhn are gratefully acknowledged.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, University College, London, W.C.1. [Received, August 19th, 1958.]

¹⁰ This follows, for instance, from a comparison with suitable reference substances; see e.g., Naylor and Whiting, J., 1955, 3037.