200. *Electrical Conductance and Dissociation Constants of Ion-pairs formed by Proton Transfer to Conjugated Polyenes.*

By ALBERT WASSERMANN.

There is a linear logarithmic relationship between the molar electrical conductance and the concentration of ion pairs formed in benzene solution from conjugated polyenes and proton donors. The dissociation constants, K_d, of the ion pairs and limiting conductances are calculated, and a qualitative explanation for the relatively large K_d values is given.

SOME electrochemical properties of ion-pairs formed by proton transfer to conjugated polyenes in benzene have been described;[1,2] there is a linear logarithmic relationship between molar electrical conductance and concentration, up to the most concentrated solutions that could be tested. These observations enable one to calculate dissociation constants, K_d, of these ion-pairs by methods now to be described. The numerical values of K_d are in accordance with conclusions derived from the electronic spectra of these polyenes.

Calculation of Dissociation Constants.—The ion-pairs $C^+ \ldots D^-$ here considered are formed by the reaction $A + B \rightleftharpoons C^+ \ldots D^-$, where A is the proton donor and B is the polyene; the association constant is K', numerical values of which have been given.[1,2] The dissociation of the ion-pairs

$$C^+ \ldots D^- \rightleftharpoons C^+ + D^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

can be characterised by a constant, K_d, defined by

$$K_d = \frac{[C^+][D^+]}{[C^+ \ldots D^-]} \times \frac{f_{C^+} \times f_D}{f_{C^+ \ldots D^-}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The proton donor dissociates according to

$$A \rightleftharpoons H^+ + D^- \text{ (equilibrium constant } K_A) \quad . \quad . \quad . \quad . \quad (3)$$

where

$$K_A = \frac{[H^+][D^-]}{[A]} \times \frac{f_{A^+} f_{D^-}}{f_A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the f's in eqns. (2) and (4) being the activity coefficients of the species indicated by the subscripts. All degrees of dissociation being assumed to be small and the activity-coefficient ratios to be unity, it can be shown that

$$K_d = \{[C^+]^2/2 + [C^+]\sqrt{([C^+]^2/4 + [A]K_A)}\}/[C^+ \ldots D^-] \quad . \quad . \quad (5)$$

If it is postulated that

$$[C^+]^2/4 \gg [A]K_A \text{ and } (K_d[C^+ \ldots D^-])/4 \gg [A]K_A \quad . \quad . \quad . \quad (6)$$

it follows that $[C^+] = [D^-] = K_d\sqrt{}[C^+ \ldots D^-]$, inequality (6) thus indicating that the dissociation of A is not significant compared to that of $C^+ \ldots D^-$. For the systems here considered inequality (6) is fulfilled if $K_A \leqslant 10^{-14}$ mole/l. This is a reasonable supposition because the constants

$$K_2 = [M^+][X^-]/[M^+X^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

relating to the dissociation of substituted ammonium salts, M^+X^-, are between 10^{-17} and 10^{-20} mole/l. in benzene solution[3,4] and it is probable that the dissociation constant of a salt is larger than that of a carboxylic acid. It is assumed, therefore, that the significant

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[1] Wassermann, *J.*, 1954, 4329; 1955, 585; 1958, 1014, 3228.

[2] *Idem, ibid.*, two preceding papers; *Mol. Phys.*, 1959, in the press.

[3] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 2387, 3614.

[4] Hughes, Ingold, Patai, and Pocker, *J.*, 1957, 1206.

species responsible for the conductance of the polyene salts are C^+ and D^-, formed by reaction (1). The postulated small dissociation of the proton donor A is in accordance with the observation that the specific electrical conductance of trichloroacetic acid [1] and of the other proton donors in benzene is relatively small if proton acceptors are absent; and with the results of the experiments described below in which the concentration of A was varied.

Bearing in mind the other two assumptions already mentioned, we can estimate the dissociation constant K_d, from

$$\log_{10} \Lambda = -\tfrac{1}{2} \log_{10} c + \tfrac{1}{2}(\log_{10} K_d + 2 \log_{10} \Lambda_0) \qquad . \quad . \quad . \quad (8)$$

where Λ_0 is the limiting conductance of $C^+ \ldots D^-$, c is the concentration of $C^+ \ldots D^-$, and Λ is the molar electrical conductance (l. mole^{-1} ohm^{-1} cm.$^{-1}$) at concentration c. If, therefore, log Λ is plotted against log c, a straight line should result with slope $-\frac{1}{2}$ and intercept $\frac{1}{2}(\log K_d + 2 \log \Lambda_0)$.

The ion pairs here considered were prepared from the polyenes and proton donors listed in columns 2 and 3 of the Table. The linearity of the log Λ–log c relationship in the concentration range indicated in the fifth column of the Table has already been demonstrated [1] for the systems Nos. 1—6. Similar linear relationships obtain for the systems Nos. 7 and 8, which follow from the relevant data in ref. 2. The slopes of the log Λ–log c graphs are given in the seventh column of Table 1, the deviation from the theoretical value, —0·5, being within experimental error. In order to obtain K_d from the intercepts of the log Λ–log c graphs, -log Λ_0 is estimated by plotting -log$_{10}$ Λ against $c^{\frac{1}{2}}$ and by extrapolating the resulting smooth curves to $c^{\frac{1}{2}} = 0$. Two typical plots are shown in Fig. 1. In all systems, -log$_{10}$ Λ_0 was 3·0 ± 0·5, except for the β-carotene–picric acid adduct, where it was 4·5 ± 1·0. log$_{10}$ K_d of these ion-pairs is in the last column of the Table.

Dissociation constants of ion pairs formed by proton transfer to conjugated polyenes in benzene at 25·0°.

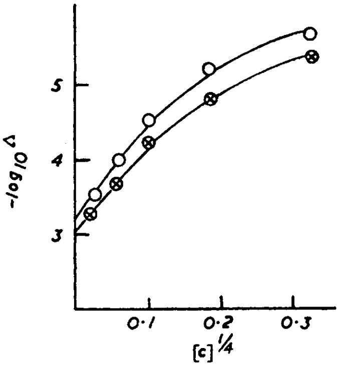
No.	Polyene	Proton donor	Concn. of proton donor (mole/l.)	Range of $-\log_{10} c$ (c in (mole/l.)	No. of concns. tested	Slope of log Λ_c–log c graph	$-\log_{10} K_d$ (K_d in mole/l.)
1	*β*-Carotene *	$CCl_3{\cdot}CO_2H$	1·00	2—6·5	16 †	−0·57 ± 0·07	8·0 ± 0·5
2		$CHCl_2{\cdot}CO_2H$	1·00	4—7	4	−0·54 ± 0·1	8·0 ± 1·0
3		Picric acid	0·121	3—6	4	−0·60 ± 0·1	9·4 ± 1·5
4	Azulene	$CCl_3{\cdot}CO_2H$	1·00	2—5	9	0·50 ± 0·05	8·0 ± 0·5
5		$CHCl_2{\cdot}CO_2H$	1·00	4·3—5·5	3	−0·48 ± 0·10	9·8 ± 1·5
6	*p*-Methoxy cinnamaldehyde	$CCl_3{\cdot}CO_2H$	1·00	2—5	4	−0·58 ± 0·10	12·8 ± 1·0
7	Vitamin-A acetate *		1·00	2—4	4	−0·60 ± 0·10	8·8 ± 1·0
8	Lycopene *		1·00	2—6	4	−0·60 ± 0·10	8·2 ± 1·0

* Formulæ are given, for instance, in Zechmeister, " Carotinoide," Springer, Berlin, 1934.

† 12 concentrations are shown in Fig. 7, *J.*, 1954, 4329; 4 more concentrations were now measured.

These dissociation constants relate to benzene–cosolvent mixtures, *e.g.*, to a benzene solution 1M with respect to trichloroacetic acid. It could be suggested that the numerical value of K_d is influenced by the cosolvent, even if eqn. (3) does not contribute a significant number of carriers of the current. Experiments were carried out, therefore, with the β-carotene–trichloroacetic acid adduct, in which the molar conductance of the ion-pairs was measured, while both the trichloroacetic acid and the ion-pair concentrations were varied. Fig. 2 shows a typical set of results relating to constant ion-pair concentration, c, and to varying acid concentrations, [A]. As log Λ is a linear function of [A], within experimental error, a linear extrapolation to $[A] \longrightarrow 0$ enables one to estimate log $\Lambda^{[A] \longrightarrow 0}$ for the specified ion-pair concentration, c. Similarly log $\Lambda^{[A] \longrightarrow 0}$ was estimated for other c values, the results of all these measurements being shown in Fig. 3; it is a linear function of log c, the slope of the straight line being $-0{\cdot}43 \pm 0{\cdot}10$. Extrapolation of a plot of $-\log_{10}(\Lambda^{[A]\rightarrow 0})$ against $c^{\frac{1}{4}}$ to $c^{\frac{1}{4}} = 0$ indicates that $-\log(\Lambda_0^{[A]\rightarrow 0})$ is $3{\cdot}0 \pm 0{\cdot}5$, $\Lambda_0^{[A]\rightarrow 0}$ being in the same units as the other Λ_0 and Λ values. It follows therefore, from eqn. (9) and the intercept of Fig. 3, that $-\log_{10}(K_d^{[A]\rightarrow 0}) = 8{\cdot}2 \pm 0{\cdot}7$, $K_d^{[A]\rightarrow 0}$ being in mole/l. This value agrees, within the limits of the experimental errors, with $-\log K_d$ in the first row of Table 1, and it appears that the cosolvent does not alter the order of magnitude of this dissociation constant.

FIG. 1. *Calculation of limiting conductance, Λ_0, of ion-pairs formed by proton transfer to conjugated polyenes.*



Benzene solution, 25°. Proton donor = trichloroacetic acid, 1·00 mole/l. ○ = Lycopene; ⊗ = β-carotene.

FIG. 3. *Molar electrical conductance, $\Lambda^{[A]\rightarrow 0}$, of β-carotene–trichloroacetic acid adduct, $C^+ \ldots D^-$, extrapolated to zero trichloroacetic acid concentration in benzene solution at 25·0°.*

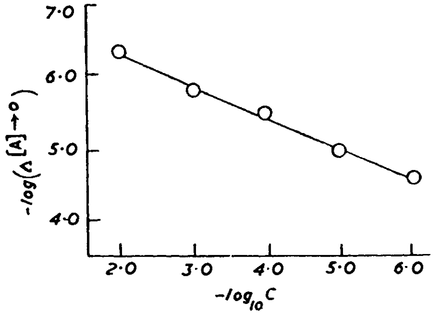
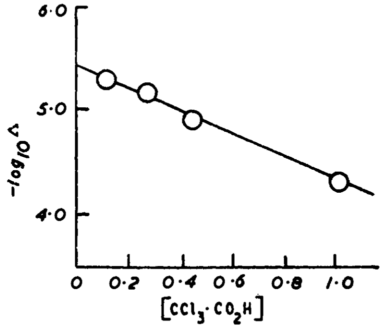
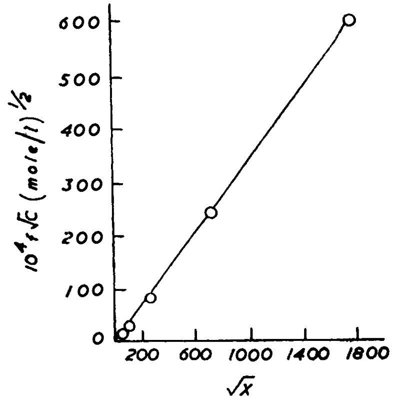


FIG. 2. *Molar electrical conductance, Λ, of β-carotene–trichloroacetic acid adduct, $C^+ \ldots D^-$, in benzene at 25·0°.*



$[C^+ \ldots D^-] = 1{\cdot}00 \times 10^{-4}$ mole/l. in all tests.

FIG. 4. *Calculation of dissociation constant of ion-pairs formed by proton transfer from trichloroacetic acid to β-carotene in benzene solution at 25·0°.*



There are two possible objections: the activity-coefficient ratio in eqn. (2) has been assumed to be unity and the estimation of Λ_0 is based on empirical extrapolation. For these reasons, $K_d^{[A]\rightarrow 0}$ for β-carotene–trichloroacetic acid has also been calculated by a convergent approximation method, described by Fuoss and Kraus,[5] in which a function $\sqrt{X} = \sqrt{[(1-\gamma)/\gamma]}$ is plotted against $f\sqrt{c}$, where γ is the degree of dissociation of an ion-pair, f is an activity coefficient, and c is the concentration of the ion-pair. Values of $\Lambda^{[A]\rightarrow 0}$ from Fig. 3, $\Lambda_0^{[A]\rightarrow 0} = 1{\cdot}0 \times 10^{-3}$ l. mole^{-1} ohm^{-1} cm.$^{-1}$, and an f value calculated as by Fuoss and Kraus [5] (with an a value, assumed to be the minimum counter-ion distance, given below) being used, Fig. 4 was obtained. The straight line passes the

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[5] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476.

origin, thereby indicating[5] that $\Lambda_0^{[A]\rightarrow 0}$ has been correctly estimated. The slope of the graph in Fig. 4, $\sqrt{K_d^{[A]\rightarrow 0}}$, is $3{\cdot}19 \times 10^{-5}$ $(\text{mole/l.})^{\frac{1}{2}}$, which agrees, within experimental error, with the value obtained by the alternative method. This value can be used to calculate that the minimum counter-ion distance[6] is 13·2 Å.

Discussion.—It has been mentioned that the constants, K_2, of substituted ammonium salts in benzene are between 10^{-17} and 10^{-20} mole/l., while the K_d values of the polyene salts are between 10^{-6} and 10^{-13} mole/l., as shown in the last column of the Table. In the cation M^+ of the ammonium salts the positive charge must be localised on the electronegative nitrogen atom, and in most of the mesomeric polyene cations the charge is probably spread over the conjugated double bonds.[1,2] It is suggested, therefore, that the cation C^+, formed in reaction (1), is characterised by a relatively small charge density, and that this accounts for K_d being larger than K_2. The charge density of the various polyene cations, however, is not equally low: spectroscopy[2] indicates that the positive charge of the cation derived from *p*-methoxycinnamaldehyde is somewhat localised near the carbonyl oxygen. It is not surprising, therefore, that the K_d value in the sixth line of Table 1 is smaller than the dissociation constants of the other polyene adducts, although it is still larger than the K_2 values relating to the substituted ammonium salts.

The latter species are characterised by conductance minima in benzene solution,[3,4] the concentration, $c_{\text{min.}}$, being in most cases between 10^{-3} and 10^{-5}M. Fuoss and Kraus[3] showed that the minima are brought about by the formation of triple ion $\overset{+}{M}\overset{-}{X}\overset{+}{M}$ or $\overset{-}{X}\overset{+}{M}\overset{-}{X}$, the constant

$$K_3 = [\overset{+}{M}\overset{-}{X}][\overset{-}{X}]/[\overset{-}{X}\overset{+}{M}\overset{-}{X}] = [\overset{+}{M}\overset{-}{X}][\overset{-}{M}]/[\overset{+}{M}\overset{-}{X}\overset{+}{M}]$$

being approximately $c_{\text{min.}}/3$. The relatively small charge density of the polyene cation is probably responsible for K_3 being so large that $c_{\text{min.}}$ cannot be observed in the concentration range specified in the fifth column of Table 1.

Using Walden's rule,[7] Fuoss and Kraus[8] estimated that the limiting conductance of substituted ammonium salts in benzene solution at 25° is 0·1 l. mole^{-1} ohm^{-1} cm.$^{-1}$, which is about 100 times larger than the Λ_0 values of most of the polyene salts. The discrepancy may be due to the fact that the polyene cations are less symmetrical, thereby making Walden's rule, based on measurements with substituted ammonium salts, not applicable.

Experimental.—The K_d values in the Table were calculated from earlier results,[1,2] but Figs. 2—4 are from new experiments. In each run the ion-pair concentration, *c*, had to be computed from stoicheiometric concentrations, with the help of the association constants, K', defined and measured as before.[1] Some new K' values were determined with a special silica cell of 0·1 cm. optical path length. Purification of reagents and the experimental technique have been described.[1] A few experiments, from which moisture was carefully excluded, were done as follows. A film of trichloroacetic acid, prepared by removal of solvent *in vacuo*, was dried at a pressure of less than 0·1 mm. at about 30°. It was dissolved *in vacuo* in dry benzene and filled through a greaseless tap into a conductance cell constructed for high vacuum work, a dry β-carotene solution being also added through greaseless taps. Λ so obtained agreed to within ±10% with the results of measurements in which moisture was not so carefully excluded.

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

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[6] Bjerrum, *Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9; Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 1019.

[7] See Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1950, pages 183—186.

[8] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 3618.