Proton-acceptor Properties of Azulene.

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Spectrophotometric and conductometric measurements show that the interaction between tri- and di-chloroacetic acid and azulene in benzene solution involves a proton transfer. The reactions are characterised by equilibrium coefficients, which have been determined within a temperature range of about 40°. The entropy change accompanying the transfer of the proton from the acid to azulene appears to be negative, as in other processes in which the net electrostatic charge increases in passing from the initial to the final state.

AZULENE is a proton acceptor (Plattner, Heilbronner, and Weber, *Helv. Chim. Acta*, 1952, **35**, 1036, and references therein) but constants, K, of the equilibrium

$$n \text{ Acid (A)} + \text{Azulene (B)} \rightleftharpoons \text{Azulene–acid adduct} \quad . \quad . \quad . \quad (1)$$

have not yet been measured. The equilibrium constants for the interaction of tri- and di-chloroacetic acid with azulene, in benzene solution, and the molar electrical conductivities of the adducts have now been determined, and some of the results are correlated below with the basic properties of carotene (Wassermann, *J.*, 1954, 4329).

EXPERIMENTAL AND RESULTS

Azulene, m. p. 100—102°, was purified by way of the sulphate, chromatographically and by sublimation. The purification of the solvents and chloroacetic acids, and the spectrophotometric and the conductometric techniques, have been described previously (Wassermann, *loc. cit.*). A time-dependence of optical density or of electrical resistance of solutions containing azulene and an acid was eliminated by extrapolation back to the time of mixing.

The light absorption of azulene in benzene solution, without and with the chloroacetic acids, is shown in Fig. 1. The effects are markedly different for the two ranges 320—400 and 400—700 mμ; in the former range the addition of acids brings about an increase of the molar light absorption coefficient, ε, and a shift of $\lambda_{\text{max.}}$ to longer wave-lengths, while in the latter range the light absorption is decreased. These changes are due to conversion of azulene into the chloroacetic acid adducts, similar effects with sulphuric acid having been described by Plattner *et al.* (*loc. cit.*) and by Chopard-Dit-Jean and Heilbronner (*Helv. Chim. Acta*, 1952, **35**, 2170). Ethyl trichloroacetate, in contrast to the free acid, does not alter the light absorption of azulene to any significant extent.

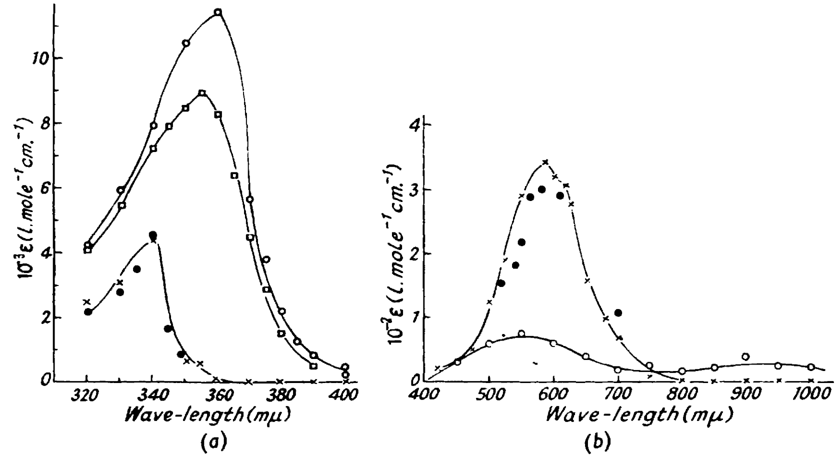
The constant, K, of equilibrium (1) is defined by :

$$K = \frac{[\text{Adduct}]}{[\text{A}][\text{B}]} \cdot \frac{f_{\text{Adduct}}}{f_{\text{A}} f_{\text{B}}} = K' \cdot \frac{f_{\text{Adduct}}}{f_{\text{A}} f_{\text{B}}} = \frac{d_{\text{A}} - d_{\text{B}}}{d_{\infty} - d_{\text{A}}} \cdot \frac{1}{[\text{A}]} \cdot \frac{f_{\text{Adduct}}}{f_{\text{A}} f_{\text{B}}} \quad . \quad . \quad . \quad (2)$$

where the meanings of symbols are as in Wassermann's equation (2) (*loc. cit.*), except that B refers here to the " free " azulene. It is assumed, as previously, that n in equation (1) is unity and that the species in the adduct are held firmly together by electrostatic forces. As the ratio [Adduct]/[B] was varied, K' decreased with decreasing acid concentration. In order to estimate K the empirical extrapolation method described previously was employed.

The complete conversion of azulene into the chloroacetic acid adducts, indicated by a limiting value of the optical density, is shown by the typical graphs in Fig. 2. The equilibrium measurements were done with light of 360 or 370 mμ, because at these wave-lengths the light absorption of " free " azulene is not significant, while that of the acid adducts is sufficiently large and in most cases not time-dependent during the first 15—20 min. Attempts were made to carry out equilibrium measurements with light of 600 mμ; however, relatively concentrated solutions have then to be used, and the optical densities are so strongly dependent on time that " back-extrapolation " is not sufficiently accurate. A typical graph showing the dependence of log K' on the acid concentration is in Fig. 3 and the results of the equilibrium measurements are in Tables 1 and 2.

FIG. 1*a*—*b*. *Light absorption of azulene without and with chloroacetic acids in benzene solution at* 20°. [Here and below the molar light absorption coefficient, ε, is as defined by Wasserman (*loc. cit.*).]

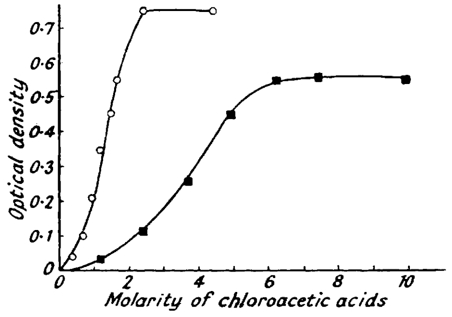


× Azulene without acid. ○ Azulene in 2·30M-trichloroacetic acid (azulene completely converted into the adduct). In both sets of experiments the validity of Beer's law was established in the concentration range 1·00—29·2 × 10^{-5} mole of azulene per l.

□ Azulene in 2.30M-dichloroacetic acid (azulene partly converted into the adduct).

● Azulene in 1·51M-ethyl trichloroacetate.

FIG. 2. *Influence of concentration of the two chloroacetic acids on optical density at* 370 mμ, *of benzene solutions of azulene*; 20°; *optical path length* 1·00 *cm.*



○ Trichloroacetic acid; azulene concn. 1·46 × 10^{-4}M.

■ Dichloroacetic acid; azulene concn. 1·24 × 10^{-4}M.

FIG. 3. *Influence of trichloroacetic acid concentration on* log *K'*. *Solvent benzene*; 49·0°.

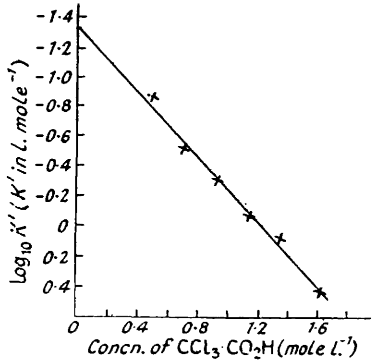
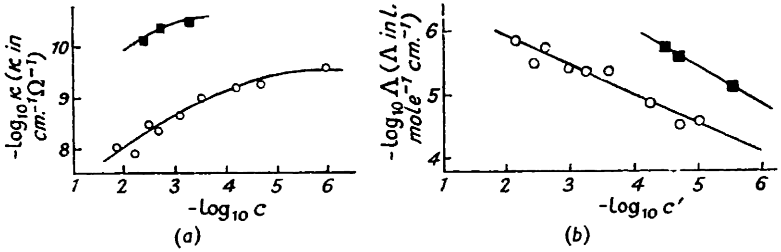


FIG. 4*a*—*b*. *Electrical conductance of azulene in presence of chloroacetic acids*; *solvent benzene*; 25·0°.



κ = Specific electrical conductance of solutions containing both azulene and the chloroacetic acids, extrapolated back to the time of mixing and corrected for specific electrical conductance of the acid without azulene.

c = " Stoicheiometric " azulene concn. (mole l.$^{-1}$).

Λ = Molar electrical conductance of azulene–chloroacetic acid adducts.

c' = Concn. (mole l.$^{-1}$) of azulene–chloroacetic acid adducts.

○ 1·00M-Trichloroacetic acid.

■ 1·00M-Dichloroacetic acid.

Plots of the logarithm of the specific electrical conductance, κ, of solutions containing azulene and acid against the logarithm of the " total " (stoicheiometric) azulene concentration are on the left-hand side of Fig. 4. These values of κ are corrected for the specific electrical conductance of 1·00M-tri- and -di-chloroacetic acid without azulene (4·30 × 10^{-10} and 0·34 × 10^{-10} Ω^{-1} cm.$^{-1}$). The κ value of azulene without acid was so small that the contribution of " free " azulene to the over-all specific electrical conductance could be neglected. By using the results of the equilibrium measurements, the concentration, c', of the azulene–acid adducts was calculated; the molar electrical conductivities, λ, are obtained by dividing the corrected κ values by c'. Plots of log Λ against log c' are on the right-hand side of Fig. 4.

TABLE 1. *Equilibrium between azulene and chloroacetic acids in benzene solution.*

Acid	Concn. of acid (mole l.$^{-1}$)	Concn. of azulene * (10^{-5} mole l.$^{-1}$)	Temp.	No. of runs	K (l. mole^{-1})
Trichloroacetic acid ...	0·460—4·37	29·2	20—21°	9	0·08 ± 0·01
	0·460—4·37	14·6		8	0·08 ± 0·01
	0·460—2·76	4·98		9	0·10 ± 0·01
	0·276—2·30	3·65	18—19	9	0·08 ± 0·01
	0·230—4·14	14·6	8·5	9	0·09 ± 0·01
	0·460—2·30	14·6	35	7	0·06 ± 0·01
	0·460—2·30	14·6	49	7	0·05 ± 0·01
Dichloroacetic acid ...	2·44—6·10	19·0	11	6	0·010 ± 0·002
	1·22—9·76	12·4	17	7	0·010 ± 0·003
	2·44—6·10	19·0	35	5	0·0089 ± 0·002
	2·44—9·76	19·0	49	6	0·010 ± 0·002

* " Stoicheiometric " concns.

TABLE 2. *Influence of added proton acceptors on optical density of a benzene solution of azulene and trichloroacetic acid.*

Temp. 17°; optical path length 1·00 cm.; azulene and trichloroacetic acid concns. respectively 7·00 × 10^{-5} and 2·30 mole l.$^{-1}$.

Added proton acceptor (mole l.$^{-1}$)	Optical density (360 mμ)	Added proton acceptor (mole l.$^{-1}$)	Optical density (360 mμ)
None	0·72	Dioxan (0·467)	0·63
Acetone (4·10)	0·25	(0·720)	0·46
Ethyl alcohol (5·15)	0·08	(0·934)	0·30
		(1·87)	0·05

DISCUSSION.

A proton-transfer mechanism of reaction (1) is consistent with the fact that the K values (Table 1) decrease from trichloroacetic acid to the weaker dichloroacetic acid. It explains, moreover, why the optical density of a benzene solution containing azulene and trichloroacetic acid decreases on addition of basic solvents (see Table 2) : this must be brought about by a competition of azulene and the added base for the proton from the acid. The basicity of azulene, like that of carotene, is regarded as being due to the π-electrons of the conjugated double bonds. Comparison of Tables 1 of the earlier paper and of this paper show the ratio K (carotene)/K(azulene) exceeds unity for both tri- and di-chloroacetic acid.

This mechanism for reaction (1) is proved by the marked electrical conductivity of the azulene–chloroacetic acid adducts in benzene solution, control experiments having established that the electrical conductivity of solutions containing either the acid or the azulene alone is generally not significant. Comparison of the relevant curves of Fig. 4 of this paper, with the curves in Fig. 7 of the earlier work shows that the molar electrical conductivities of the chloroacetic acid–azulene and the carotene adducts are of the same order of magnitude, the former having the lower electrical conductivity.

The experimental errors of the K values in Table 1 are roughly estimated to be 20—30%. Neither here nor in Table 3 have the standard deviations been computed from the most probable values. As the temperature dependence of K is small, it is obvious that accurate values of the heat and the entropy change of these proton transfer reactions cannot be deduced from the results so far obtained. The values in Table 3 indicate, however, that

TABLE 3. *Heat and entropy changes of proton-transfer processes to unsaturated hydrocarbons.* Solvent, benzene. Temp. range 10—50°.

Hydrocarbon	Proton donor	$-\Delta H$ (kcal.)	ΔS (cal. deg.$^{-1}$)
Carotene *	$CCl_3{\cdot}CO_2H$	$2{\cdot}0 \pm 1{\cdot}8$ *	-9 ± 7 *
Azulene	$CCl_3{\cdot}CO_2H$	$3{\cdot}0 \pm 2{\cdot}0$	-15 ± 7
	$CCl_2{\cdot}CO_2H$	$0{\cdot}0 \pm 2{\cdot}0$	-9 ± 7

* Taken from Wassermann (*loc. cit.*).

the numerical value of $-\Delta H$ is positive, which means that the transfer of the proton is exothermic; and that the corresponding entropy change is negative, as in other processes in which the net electrostatic charge increases on passing from the initial to the final state.

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