

TABLE I
PARAMETERS a_{ij} AND b_{ij} FROM EQ. 2 INCLUDING NOBLE GAS
CLUSTERS BUT OMITTING HOMONUCLEAR ALKALI METAL
MOLECULES

	H	1	2	3	4	3T	4T
a_{ij}							
H	1.18	1.46	1.74	1.82	1.96	1.71	1.81
1		1.85	2.06	2.15	2.28	2.12	2.22
2			2.36	2.45	2.62		
3				2.57	2.71		
4					2.87		
b_{ij}							
H	0.58	0.56	0.64	0.66	0.72	0.71	0.78
1		0.55	0.63	0.64	0.70	0.72	0.73
2			0.70	0.73	0.79		
3				0.74	0.81		
4					0.87		

as X in Fig. 1. In each case the noble gas cluster and the ordinary molecules lie close to a single straight line.

Similarly, all molecules from ref. 2 and 5 were plotted, such as H-2, 1-2, 2-3, 3-4, etc. The parameters a_{ij} and b_{ij} of eq. 2 for all cases are given in Table I. It can be seen that these terms vary slowly and smoothly over the periodic table. The constant b_{ij} is closely related to Pauling's constant 0.6, which defines bond order in terms of bond length.⁶ When b_{ij} is 0.6 (it almost always is close to this value) then the force constant is directly proportional to Pauling's bond order.

On very tenuous grounds, a similar correlation between dissociation energy and bond length was recently proposed.⁷ The present correlation between force constants and bond lengths is much more heavily documented and much more nearly convincing. This striking evidence for continuity of bonding for all types of bonds may be taken as support for the previous⁶ postulate, which interpolated bond energies between that for noble gas pairs and that for ordinary single-bonded molecules.⁸

(6) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(7) H. S. Johnston and C. Parr, *ibid.*, **85**, 2544 (1963).

(8) This research was supported by NSF Grant G-20976.

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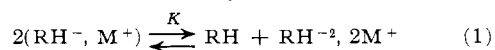
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Electron Transfer Equilibria.

III. Disproportionation of Monoalkali Adducts of Stilbene¹

Sir:

The previously reported behavior of the monoalkali adducts of stilbene suggests that they show little tendency to disproportionate (eq. 1).²⁻⁴ We have found that by proper choice of solvent and metal ion the range of K can be made to vary from $<10^{-3}$ to $>10^3$.



As in the case of the alkali metal adducts of tetraphenylethylene,^{1,5} the disproportionation constant is a

(1) (a) Part I: J. F. Garst and R. S. Cole, *J. Am. Chem. Soc.*, **84**, 4352 (1962); (b) part II: J. F. Garst, E. R. Zabolotny, and R. S. Cole, *ibid.*, in press.

(2) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

(3) K. Morigaki, K. Kuwata, and K. Hirota, *Bull. Chem. Soc. Japan*, **33**, 958 (1960).

(4) J. W. B. Reesor, J. G. Smith, and G. F. Wright, *J. Org. Chem.*, **19**, 940 (1954).

TABLE I

DISPROPORTIONATION CONSTANTS OF MONOALKALI STILBENES

Metal	Diethyl ether	Dioxane	2-MeTHF	THF
Li	$>10^3$	NR ^a	$>10^3$	$<10^{-3}$
Na	NR ^c	20	0.1	$<10^{-3c}$
K	NR	NR	Small ^b	Small ^b

^a No reaction could be visually detected. The surface of the metal was not discolored. ^b Dilute solutions only could be formed. The spectra appeared to be that of the monoalkali adduct only. ^c A disproportionation constant near 1 could be obtained in an ether-rich solvent mixture of diethyl ether and tetrahydrofuran.

sensitive function of the solvent and metal ion employed. However, a metal ion effect in the opposite direction from that observed with tetraphenylethylene is noted, increasing cationic radius leading to smaller, rather than larger, values of K . These results are detailed in Table I.

Three important conclusions are suggested by these observations: (1) Although there is a distinct quantitative difference between K for tetraphenylethylene and that for stilbene, under comparable conditions, it now appears that the same *kind* of disproportionation behavior for both and that the same kinds of structural and environmental factors influence K in each case. The pronounced influence of variation of solvent and metal ion, among ethers and alkali metals, is again emphasized by the stilbene data, suggesting that an observed value of K depends on a rather delicate balancing of ionic aggregation and solvation effects to which K is very sensitive.

(2) For a substituted olefin, the presence of steric strain in the hydrocarbon (present in tetraphenylethylene, absent in stilbene) is *not* a necessary condition for disproportionation of a monoalkali adduct to a directly measurable extent. It is quite possible, however, that the quantitative difference between the disproportionation behavior of stilbene and tetraphenylethylene is a reflection of a change in the geometries of the carbon skeletons of the dialkali adducts, relative to the monoalkali adducts and hydrocarbons.⁶ The disproportionation of monoalkali tetraphenylethylenes, but not monoalkali stilbenes, might then be accompanied by relief of steric strain,⁷ accounting for the relative magnitudes of K .

(3) If the same kinds of metal ion effects are to be invoked in both the stilbene and tetraphenylethylene cases, the observation of opposing directions of metal ion effects requires the operation of at least two opposing effects. One likely possibility considers the effects of ionic aggregation (considered as if in the gas phase) and those of ion and/or ion aggregate solvation as a pair of such opposing effects. In the gas phase, association of the metal ions with RH^- and RH^{-2} to give ion pairs and triple ions, respectively, should favor (coulombically) larger values of K , smaller cationic radii leading to larger values of K than larger cationic radii. On the other hand, ion pairs should be more

(5) A. G. Evans and B. J. Tabner, *J. Chem. Soc.*, 4613 (1963).

(6) (a) D. W. Ovenall and D. H. Whiffen, Chemical Society Special Publication No. 12, 1958, p. 139; (b) discussion of M. J. S. Dewar, *ibid.*, p. 164; (c) discussion of N. S. Hush, *ibid.*, p. 164; (d) discussion of P. Gray, *ibid.*, p. 166.

(7) The situation would then resemble that proposed for the alkali adducts of cyclooctatetraene, for which K is large, except that the roles of hydrocarbons and the dialkali adducts, insofar as strain is concerned, would be interchanged.⁸

(8) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).

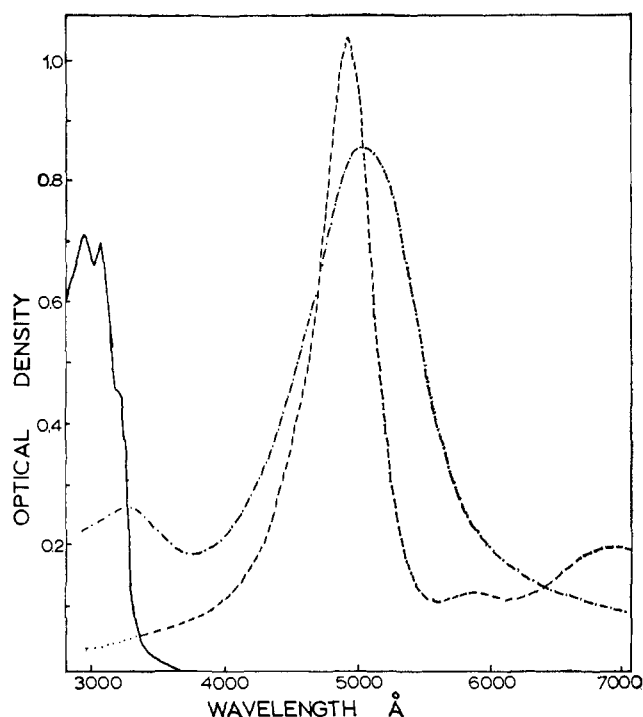


Fig. 1.—Visible and near-ultraviolet spectra of stilbene (—), stilbene⁻ (---), and stilbene⁻² (-·-·-). Cation and solvent effects on the spectra were small. The ratios of the heights of the various peaks attributed to stilbene⁻ were constant with changing temperature and exhibited only minor variations with solvent and metal ion. The following extinction coefficients were employed in the calculations: stilbene (3050 Å.), 2.95×10^4 ; stilbene⁻ (4800 Å.), 6.21×10^4 ; stilbene⁻ (5600 Å.), 0.80×10^4 ; stilbene⁻² (4800 Å.), 3.28×10^4 ; stilbene⁻² (5600 Å.), 1.49×10^4 . These values were obtained directly in experiments involving careful mass balancing and were reproducible with a variation of about $\pm 3\%$.

strongly solvated than triple ions,^{1b,5} the difference being greater for cations of smaller radii, leading to a trend to smaller K with decreasing cationic radii. Both effects, in opposite directions, should operate in solution. The directions of the effects can be similarly rationalized if ionic association is incomplete, but the arguments are slightly more complex.

The quantitative measurements were spectrophotometric. Figure 1 gives the forms of the spectra of stilbene, stilbene⁻, and stilbene⁻² in tetrahydrofuran, 2-methyltetrahydrofuran, and 1,2-dimethoxyethane. By suitable choices of solvent, metal ion, and amount of metal allowed to react with the stilbene, extinction coefficients for all three species could be directly determined. These appeared to be rather insensitive to solvent variation. K was calculated directly from the equilibrium expression and was sensibly constant for a given solvent and metal ion. The concentrations of hydrocarbons and ions employed in these experiments ranged about 10^{-4} M. All experiments were done at room temperature.

Corresponding equilibria for triphenylethylene have been observed in 1,2-dimethoxyethane, tetrahydrofuran, and dioxane, with the disproportionation constants (sodium cation) being $<10^{-3}$, of the order of 10, and $>10^3$, respectively. In general the value of K for triphenylethylene appears to be intermediate between that for stilbene and that for tetraphenylethylene, a trend which is consistent with the operation of a steric effect favoring disproportionation of the monoalkali ad-

ducts. More explicit tests of the steric effect are in progress.

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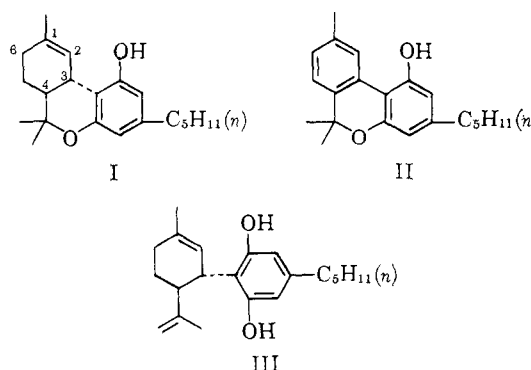
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Isolation, Structure, and Partial Synthesis of an Active Constituent of Hashish¹

Sir:

Hashish (marihuana), the psychotomimetically active resin of the female flowering tops of *Cannabis sativa* L. is one of the most widely used illicit narcotic drugs. A number of groups have reported the isolation of active constituents.² Most of these substances are not fully characterized, and comparisons with or between them are difficult.

We now wish to report the isolation of an active constituent of hashish to which we assign structure I (Δ^1 -3,4-*trans*-tetrahydrocannabinol).³ This is the first active component whose constitution is fully elucidated.⁴



Chromatography of a hexane extract of hashish on Florisil yielded an active fraction, which on repeated chromatography on alumina could be separated into the inactive cannabinal (II)^{2a} and the tetrahydrocannabinol (I). Further purification of the latter was achieved by the preparation of the crystalline⁵ 3,5-dinitrophenylurethane of I [m.p. 115–116°, $[\alpha]_{\text{CHCl}_3}^D -140^\circ$; *Anal.* ($\text{C}_{28}\text{H}_{33}\text{O}_7\text{N}_3$). Found: C, 64.17; H, 6.54], followed by mild basic hydrolysis to the pure tetrahydrocannabinol (I) [b.p. 155–157° (0.05 mm.); $\lambda_{\text{max}}^{\text{EtOH}}$ 300 m μ (sh) (ϵ 840), 282 (ϵ 2075), 278 (ϵ 2040), $[\alpha]_{\text{CHCl}_3}^D -150^\circ$; *Anal.* ($\text{C}_{21}\text{H}_{30}\text{O}_2$). Found: C, 80.20; H, 9.55.]. Purity was established by chromatoplate and by

(1) Hashish. Part III; for part II, see Y. Gaoni and R. Mechoulam, *Proc. Chem. Soc.*, in press.

(2) For a review of the early publications see: (a) A. R. Todd, *Experientia*, **2**, 55 (1946). For more recent work see: (b) F. Korte and H. Sieper, *Ann.*, **630**, 71 (1960); (c) R. S. de Ropp, *J. Am. Pharm. Assoc., Sci. Ed.*, **49**, 756 (1960).

(3) The hashish investigated by us contains a single tetrahydrocannabinol. Most previous reports suggest the presence of mixtures of isomers.

(4) It has been generally accepted that the active constituents are isomers of I, the position of the double bond and the stereochemistry of the asymmetric centers remaining undefined: cf. ref. 2a; also E. C. Taylor and E. J. Strojny, *J. Am. Chem. Soc.*, **82**, 5198 (1960).

(5) G. Powel, M. Salmon, T. H. Bemby, and R. P. Walton [*Science*, **93**, 522 (1941)] have described the preparation of a crystalline 3,5-dinitrophenylurethane (m.p. 216°) of an active hashish constituent. This report has not been confirmed, and since then no other crystalline derivative seems to have been described. It is possible that Powel's compound was an impure sample of the 3,5-dinitrophenylurethane of cannabinal (m.p. 233–234°).